PB80-217680

REDEQL.EPAK: Aqueous Chemical Equilibrium Computer Program

(U.S.) Corvallis Environmental Research Lab., OR

May 80

U.S. Department of Commerce
National Technical Information Service
NTIS.

United States
Environmental Protection
Agency

Environmental Research
Laboratory
Corvallis OR 97330

EPA-600/3-80-049
May 1980

PB80-217680

Research and Development

EPA

REDEQL-EPAK

Aqueous Chemical Equilibrium Computer Program

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials. Problems are assessed for their long- and short-term influences. Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects. This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial, and atmospheric environments.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-80-049		PB80-217680

4. TITLE AND SUBTITLE	5. REPORT DATE
REDEQL•EPAK, Aqueous Chemical Equilibrium Computer Program	May 1980 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Sara E. Ingle, Jim A. Keniston, D. W. Schults	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency 200 S.W. 35th Street, Corvallis, Oregon 97330	10. PROGRAM ELEMENT NO. A31B1A 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency 200 S.W. 35th Street, Corvallis, Oregon 97330	13. TYPE OF REPORT AND PERIOD COVERED In-house July 1977 - Nov.1979 14. SPONSORING AGENCY CODE EPA/600/02

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This user's guide is a companion to the previously published report A User's Guide for REDEQL.EPA which explains the use of a computerized chemical equilibrium program for metals and ligands in aqueous systems. Changes in this guide include temperature correction for equilibrium constants and activity coefficients, calculations of degree of saturation for selected solids, attainment of an electrically neutral solution, and the use of an adsorption routine. Use of the program including these modification is illustrated with a sample case of river water.

Also included in the guide are sample input data sheets and illustrations of redox reactions under various pH and redox conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chemical equilibrium Chemical speices Metals Ligands Computer program Adsorption	Oxidation-reduction Chemical Precipitation Chemical complexation Aquatic equilibra	07/B,C,D, 08/H

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980-699-121 / 193 REGION 10

EPA-600/3-80-049
May 1980

REDEQL.EPAK

Aqueous Chemical Equilibrium Computer Program

by

Sara E. Ingle
James A. Keniston
Donald W. Schults

Marine Division
Corvallis Environmental Research Laboratory
Corvallis, Oregon 97330

CORVALLIS ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97330

DISCLAIMER

This report has been reviewed by the Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its fifteen major field installations, one of which is the Corvallis Environmental Research Laboratory.

The primary mission of the Corvallis laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects, and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report describes an expanded version of a computer program (REDEQL.EPA) for determining aqueous chemical equilibria among metals and ligands under various conditions of pH, oxidation, and temperature. This book is designed to be used in conjunction with the previously published A User's Guide for REDEQL.EPA (EPA-600/3-78-024; NTIS PB 280 149/6BE).

Thomas A. Murphy, Director
Corvallis Environmental Research Laboratory

ABSTRACT

This user's guide is a companion to the previously published report A User's Guide for REDEQL.EPA (EPA-600/3-78-024) which explains the use of a computerized chemical equilibrium program for determining the equilibrium and speciation of metals and ligands in aqueous systems. Changes in this guide include temperature correction for equilibrium constants and activity coefficients, calculations of degree of saturation for selected solids, attainment of an electrically neutral solution, and the use of an adsorption routine. Application of the program including these modifications is illustrated with a sample case of river water. The program is equally appropriate for the marine environment. Also included in the guide are sample input data sheets and illustrations of redox reactions under various pH and redox conditions.

CONTENTS

	Page
Foreword	iii
Abstract	iv
List of Tables	vi
List of Figures	vi
I. Introduction	1
II. Data input	3
III. Running REDEQL.EPAK	5
IV. Temperature corrections	7
V. TOTH and pH calculations; electroneutrality	8
VI. Redox reactions	11
VII. Saturation ratios	13
VIII. Adsorption	14
IX. Internal changes in the REDEQL program	17
References	20
Table	23
Figures	28
Appendix A	45
Appendix B	Foldout

LIST OF TABLES

Number — Page

Table 1. Changes to Tables in Previous User's Guide. 23

LIST OF FIGURES

Figure 1. Flow diagram for REDEQL.EPAK 28

Figure 2a. Input data. 29

Figure 2b. Thermodynamic data at 20°C, 0.1 ionic strength. 31

Figure 2c. Thermodynamic data at 25°C shown for comparison 32

Figure 2d. Input data printout 33

Figure 2e. Case progress for first case. 34

Figure 2f. Speciation of metals for first case 35

Figure 2g. Concentration of complexes for first case 36

Figure 2h. Distribution of metals and ligands for first case 37

Figure 2i. Saturation of selected solids as log (ion product/solubility product). 37

Figure 2j. Case progress for second case 38

Figure 2k. Distribution of metals and ligands for second case. 39

Figure 2l. Distribution of metals and ligands for second case at 25°C, for comparison. 39

Figure 3. pE-pH plots of Fe, Mn and Hg species 40

Figure 4. pE-pH plots of Pb, Co, $CO_3^=$ and S species. 41

Figure 5. pE-pH plots of NH_3, H_2O_2, Sn and Fe species. 42

Figure 6. pE-pH plots of Mn, Cr and S species. 43

Figure 7. pE-pH plots of S and Cu species. 44

ACKNOWLEDGEMENT

The authors wish to thank Steven Wolf for his work in preparing plots and data supporting this manuscript. The authors also thank Drs. Thomas Theis (University of Notre Dame) and Robert Volk (University of Florida) and Daniel Krawczyk (Corvallis Environmental Research Laboratory) for their constructive comments in preparing the manuscript.

I. INTRODUCTION

There are many computer programs[1-6] available which allow the user to calculate chemical speciation at equilibrium in aquatic systems. Generally, these programs apply physical chemical principles to analytical data to calculate the distribution of species among oxidation states, associated forms and solids. REDEQL[7], a computer program developed at California Institute of Technology, has been used to determine Cu complexing capacity of natural waters[8], calculate Cd speciation in soil/water systems[9], account for the fate of trace metals in ocean discharges[10], assess the sorption and leaching of heavy metals in groundwater[11], and relate species of Cu to toxicity[12]. A few potential applications of REDEQL include the calculation of acid precipitation effects on water bodies, the determination of sorption of heavy metals onto particulate material, determination of the influence of pH or redox on the solubility of chemical components and definition of the association between heavy metals and organics such as EDTA or NTA. Obviously, results from REDEQL and similar chemical equilibrium programs are only as reliable as the analytical data and thermodynamic constants used with the program. The REDEQL program does not include kinetic considerations or mixed ligand complexes. Frequently, necessary thermodynamic data may be unavailable or inadequate; this is especially true for sorption data. In spite of these limitations, chemical computer programs can provide the user with aquatic chemistry information which may help interpret experimental results or predict chemical behavior.

EPA has modified the original REDEQL program and the use of this modified model was presented in an EPA publication entitled "A User's Guide for REDEQL.EPA"[13]. This report is a modification and updating of REDEQL.EPA (now called REDEQL.EPAK) and should be used as a companion to the original User's Guide. The modifications have been made so that input to the program remains basically unchanged from that described in the previous User's Guide; there are several optional additions and one deletion. The major computational changes in the program include temperature corrections for equilibrium constants and activity coefficients, calculation of degree of saturation for selected solids, and theoretical attainment of an electrically neutral solution for a more realistic system. These features are illustrated with a sample case of river water. A description of the "Swiss" (surface complexation) adsorption model is included.

For easier use and understanding of the program, this guide includes a flow diagram of the computational process. Outputs are more clearly labeled. Sample data sheets for input data formats are given. A discussion of TOTH (total hydrogen less total hydroxide) is included and there is an expanded section on redox reactions with illustration of the pH and redox conditions under which various reactions might be considered. Methods for calculating pE (the negative log of the electron activity, by convention) are reviewed.

Data in the thermodynamic data file have been slightly improved with updated constants appearing in the recent compilation of Smith and Martell[14]. Mercury (I) and chromate have been added to the lists of metals and ligands.

---

* Superscripts denote references listed at end of report.

For the computer programmer, the current version of the program is now documented with comment cards and accompanied by a flow diagram for the subroutines (see Foldout). Many computational changes which allow the program to execute more efficiently have been made. The basic flow of the program is shown in Figure 1. This diagram illustrates the order in which various facets of the complex equilibrium problem are considered. The basic algorithm used was described by Morel and Morgan[15].

II. DATA INPUT AND OUTPUT

The format of the input data deck described in the previous User's Guide remains unchanged except for addition of four fields to the program header card, one optional card for checking saturation of solids, and elimination of the TOTH card. The new formats for these cards are given in Table 1 under 4p Program Input Cards (the p refers to tables in the previous User's Guide). Table 1 also shows the addition of mercury (I) and chromate to Table 1p. They are included as metal 35 and ligand 59, respectively.

Use of the program, including improvements, is illustrated with input data for river water. The program can be also applied to the seawater environment. Two cases are shown: the first with insignificant quantities of EDTA (ethylenediaminetetraacetic acid) and the second with large enough amounts of EDTA to cause complexing. The sample input and output are given in Figure 2. The input data are shown in three forms in Figure 2a. The first is the analytical data to be used, Figure 2a(i). Two alternative forms of the cards are shown in Figure 2a(ii) and 2a(iii). They are equally correct. Figure 2a(ii) is easier to read; Figure 2a(iii) is easier to keypunch and would result from use of the data sheets shown in Appendix A. The 2 in column 54 of the program header card (1) signifies that saturation of two solids will be checked (see Section VII). The temperature, with one decimal place, is shown in columns 56-59 (see Section IV). Because columns 60-65 are blank and pH is fixed, ligand concentrations will be adjusted to achieve electroneutrality. In cards (3) and (4), remember the first concentration given is the guess of final free concentration, the second is the total concentration for the first case. The total concentration for the second case need not be shown if it is the same as the first case (see Section V). The two solids whose degree of saturation will be checked are identified by their metal, ligand, and solid numbers in card (10a), which follows card (10) in the user data deck.

To simplify the program, data sheets were designed with the various card fields blocked out on a grid and the decimal point appearing where appropriate. Integers should always be right justified. Use of a decimal point in any real field will override the implied decimal points shown on the data sheets. Blanks are equivalent to zero, but zero is often keypunched for ease in counting spaces or reading cards. These data sheets are shown in Appendix A. They may be reproduced for continued use.

The output from REDEQL.EPAK run with the test data from Figure 2a is shown in Figures 2b-1. Labeling of output is more complete than that of previous REDEQL versions. The temperature of the computation is shown at the top of the thermodynamic constant output (Figures 2b, 2c). The changes of total ligand concentrations are observed by comparing total concentrations shown in case progress (Figures 2e, 2j) with the total concentrations in the input data (Figure 2d). Also, the extent of changes in the ligand concentrations are reflected in the adjustment factor(s) (1.007 in this case, Figure 2e). If concentrations are repeatedly adjusted, as is usually the case, the total amount of adjustment is the product of all the adjustment factors.

The computed TOTH as well as TOTH in solution (soluble H) are given in Figure 2e. The difference between them should be the hydrogen in solids:

$$\text{TOTH} = \text{soluble H} + [\text{solid}] \times H^{+}/\text{mole solid}$$

or, in this case,

$$9.5979 \times 10^{-4} = 9.59872 \times 10^{-4} - 3 \times 1.988 \times 10^{-8} - 2 \times 9.943 \times 10^{-9}$$

The most interesting outputs for many users will be the free concentrations of metals and ligands (Figures 2e and 2j) and the distribution of metals and ligands (Figures 2h and 2k). The impact of the EDTA is readily seen in the Cu^{2+}, Zn^{2+}, and Cr^{3+} speciation.

III. RUNNING REDEQL.EPAK

There are various ways in which the program can be run depending on the computer system available. Users should check with their computer staff for aid in getting the program on line. The user input data is read from logical unit 5, the thermodynamic data file from logical unit 10, and the output is on logical unit 6. An IBM computer requires a region of 160K to run from a load module. More is required for compilation. Since IBM does not routinely use double-precision, users may find compiling with double precision to be helpful in minimizing underflows and overflows.

The new program is called .REDEQL.EPAK. The new data deck is called .THERMM. Standard IBM cards for creating a load module from the source deck and running from that load module are shown below. These cards may need modification (certainly of user number) on other IBM systems, but will be of help to systems personnel. The control cards for creating a load module are:

```
//(Job card),TIME=2,
// REGION=175K,MSGLEVEL=(1,1)
//STEPA EXEC FORTGCL,PARM,LKED='NOSOURCE,NOXREF,NOMAP'
//FORT.SYSIN DD DSN=CN.EPABAJ.CPR1.REDEQL.EPAK,
// DISP=SHR,UNIT=3330-1
//LKED.SYSLMOD  DD  DSN=CN.EPABDJ.CPR1.ZUNS(ZARRUN),DISP=(NEW,CATLG),
// UNIT=3330-1,VOL=SER=WORK51
/*
```

After the load module has been saved as shown above, the program may be used with the cards shown below. The cards call the load module and the thermodynamic data deck. The user input is read from cards.

```
//(Job card.....),TIME=2,
// REGION=160K,MSGLEVEL=(Ø,Ø)
// EXEC PGM=ZARRUN
//STEPLIB DD DSN=CN.EPABDJ.CPR1.ZUNS,DISP=SHR,UNIT=3330-1
//FTØ5FØØ1 DD DDNAME=SYSIN
//FTØ6FØØ1 DD SYSOUT=A
```

```
//FT1ØFØØ1 DD DSN=CN.EPABDJ.CPR1.THERMM,
// DISP=SHR,UNIT=3330-1
//GO.SYSIN DD *
     (Insert input cards here.)
/*
```

IV. TEMPERATURE CORRECTIONS

Two types of temperature corrections are added to the program: both activity coefficients and formation constants change with temperature. These corrections occur automatically when a temperature other than 25°C (0 reads as 25°C) is entered in field 19 of the program header card.

Allowance for linear change of formation constants with temperature has been introduced with the Van't Hoff relation:

$$\log K_T = \log K_{25} - \frac{\Delta H_{25}}{2.3R} \left(\frac{1}{T} - \frac{1}{298}\right)$$

where T represents the new Kelvin temperature and ΔH is the enthalpy change for the reaction at 25°C. Enthalpy data for solids and complexes are stored as ten times ΔH for each solid and complex in a data line following the formation constant data line for that metal-ligand combination. If any enthalpy data are available for a metal-ligand pair, a 1 (one) in column 79 of the solid and complex card (5) indicates that an enthalpy card (5a) follows. These modifications are described in Table 1 under Table 6p. The enthalpy data for the formation constant of water and carbon dioxide have been added to the solid and complex header card (4).

For activity coefficients, the temperature corrections are incorporated in the Debye-Hückel coefficient A in the Davies equation:

$$-\log \gamma = A Z^2 \left(\frac{\sqrt{I}}{\sqrt{I} + 1} - 0.2\ I\right)$$

where $A = 1.82483 \times 10^{-6} (\varepsilon T)^{3/2}$, Z is the charge on the ion, and I is the ionic strength. T is in degrees Kelvin, and ε is the dielectric constant of water[4] approximated by

$$\varepsilon = 87.74 - 0.4008\ T_C + 9.398 \times 10^{-4} T_C^2 - 1.410 \times 10^{-6} T_C^3$$

with T_C the Celsius temperature.

V. TOTH AND pH CALCULATIONS, ELECTRONEUTRALITY

REDEQL was designed to solve mass balance equations for every metal and ligand component and a mass balance equation for TOTH, total hydrogen as described in the User's Guide. In a system prepared from electrically neutral substances (compounds), the TOTH mass balance requirement is the same requirement as the electroneutrality condition:

$$\sum_{i=1}^{\text{all metals}} Z_i[M_i]_{tot} + \sum_{j=1}^{\text{all ligands}} Z_j [L_j]_{tot} + [H]_{tot} - [OH]_{tot} = 0 \qquad (1)$$

where Z_j represents the charge on species i and the concentrations are total concentrations (free plus complexed plus solid) of metals [M], ligands [L] hydrogen, and hydroxide. This equation is not valid when redox complexes or solids are present because it does not include concentrations of e- and pH should not be calculated when redox is considered with the program REDEQL.EPAK. The last two terms of equation (1) are TOTH so

$$-TOTH = \sum_{i=1}^{\text{all metals}} Z_i [M_i]_{tot} + \sum_{j=1}^{\text{all ligands}} Z_j [L_j]_{tot} \qquad (2)$$

This can be calculated from the input data for metals and ligands in the REDEQL program. It is redundant to allow input of TOTH when pH is to be calculated. The old program will solve the equilibrium problem for any given value of TOTH, but only one value can satisfy the electroneutrality requirement (2). The REDEQL.EPAK program no longer requires a TOTH card when pH is to be calculated.

The pH can only be calculated by REDEQL.EPAK when the total metal and ligand concentrations are known accurately. Field concentration data will rarely be sufficiently good to calculate pH, therefore, it is recommended that a carefully measured field pH be used with REDEQL.EPAK. On the other hand, there are two cases when pH can be calculated successfully. In a controlled laboratory situation where the system being studied is composed only of known compounds the program will work, e.g., for $NaHCO_3$, NaOH, and NaCl at known concentrations:

$$[Na]_{tot} = [NaHCO_3] + [NaOH] + [NaCl]$$

$$[CO_3]_{tot} = [NaHCO_3]$$

$$[Cl]_{tot} = [NaCl]$$

and the concentration of TOTH will be calculated according to

$$- TOTH = [Na]_{tot} - 2[CO_3]_{tot} - [Cl]_{tot} \quad (3)$$

$$= [NaHCO_3] + [NaOH] + [NaCl] - 2[NaHCO_3] - [NaCl]$$

$$= [NaOH] - [NaHCO_3] \quad (4)$$

Equation 3 is that which the computer uses to find TOTH (charge balance). Equation 4 is the way a user would calculate TOTH (total H^+ less total OH present). A second and more important instance in which pH can be calculated is in predictive modeling, particularly in cases where two aqueous solutions are to be combined. If each solution has been modeled using REDEQL.EPAK, each will be well-balanced with respect to charge (see below) and therefore any combined solution will be neutral. Therefore TOTH will be calculated correctly and the correct pH of the system can then be calculated. Reliable pH prediction has not been available in the previous model. However pH should never be predicted using this program with redox at a fixed potential because it is unlikely that pH is not known when pE is, and also because TOTH, and consequently pH, will not be calculated properly if any redox complexes or solids exist as initial components. A program which allows prediction of both pH and pE is under development.

If TOTH is no longer necessary when pH is to be calculated, then is pH necessary to the fixed pH situation? In practice, the answer to this question is, of course, yes, because pH is often known better than total metal and ligand concentrations. However, specifying total concentrations, pH, and electroneutrality leads to an over-specified system even though the user may "know" all these parameters. In the past, electroneutrality has been neglected. This often led to solutions having charges up to 50% of their ionic strength. The program discussed here can adjust one or all ligand concentrations to achieve electroneutrality within one percent of ionic strength. The check on charge relative to ionic strength is made in an external loop after all other constraints of the system have been satisfied. If the charge on the final equilibrated solution is greater than one percent of the ionic strength three options can be taken. The first, used if no other option is selected as described below, adjusts the concentration of all ligands according to:

$$[L_k]_{tot,new} = [L_k]_{tot,old} \times \frac{\sum_{i=1}^{\text{all metals}} Z_i [M_i]_{tot} + [H]_{tot} - [OH]_{tot}}{\sum_{j=1}^{\text{all ligands}} Z_j [L_j]_{tot}} \quad (5)$$

Since many ligands have hydrogen associated with them in normal pH ranges, the "positive" charge of the solution in the numerator of equation (5) increases also and several iterations are needed to achieve balance.

The second option is to adjust only one ligand concentration. This must be a ligand already present in the system. It is specified by reference number in field 20 of the program header card. Its normal charge must be specified in field 21 of the header card which means that if that ligand is normally protonated at the pH specified, the charge of the protonated form should be given, including the negative sign. The ligand must be present in sufficient amounts so that its total concentration does not become negative.

The third option is to leave the solution electrically unbalanced. This will be indicated in a warning message. This option is called by placing 100 in field 20 of the program header card.

VI. REDOX REACTIONS

When redox reactions are considered, the redox potential used, given as pE, is critical to the solution chemistry but this is a difficult parameter to determine. There is no resolution of this problem because solutions generally are not at redox equilibrium. One can determine whether a solution is oxidizing or reducing with respect to a given half reaction, but when one calculates pE from several different half reactions, the results usually disagree. The introduction of biological systems further complicates redox state because oxidation-reduction reactions in biologically active systems are often in dynamic flux. Three half reactions commonly used to determine redox potential at 25°C are iron (III)/iron (II), sulfate-sulfide, and dissolved oxygen:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$	$pE = 13.0 + \log(\{Fe^{3+}\}/\{Fe^{2+}\})$
$SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O$	$pE = 2.5 + (1/8)\log(\{SO_4^{2-}\}/\{S^{2-}\}) - pH$
$\frac{1}{2}O_2(g) + 2H^+ + 2e^- \rightarrow H_2O$	$pE = 20.8 + \log p_{O_2}/4 - pH$

The symbol { } represents activity which equals molar concentration at infinite dilution.

The metal Hg_2^{2+} and ligand CrO_4^{2-} were added to the list of available species so that they could complex with other ligands and metals. Formerly they were treated as redox complexation products. These changes transformed reaction 4 from type 3 to -10, eliminated reactions 16 and 17 because $HCrO_4^-$ and $Cr_2O_7^{2-}$ are complexes of chromate and hydrogen, and changed reaction 18 to type -11 (Table 2p). This is a new reaction type recognized by the program for metal-to-ligand redox. The ligand for reaction 18 becomes 59 (CrO_4^{2-}) rather than 99 (OH-). The stoichiometry of the first species in the metal-metal, metal-ligand, or ligand-ligand reaction must be given, e.g. <u>two</u> mercury (II) atoms produce one mercury (I) ion, Hg_2^{2+}. This means that field 8, columns 36-40, of the redox reaction cards is <u>always</u> the stoichiometric coefficient of the ion given in field 2 (Table 6p).

To help the user evaluate which redox equations to use under given circumstances, pE-pH plots of relative activities of primary species for most of the redox equations available are shown in Figures 3 to 7. The purpose of these plots is to illustrate in what pE-pH regions redox reactions should be considered. In the areas outside the curves, redox is probably not necessary and may lead to computational problems in program execution.

For a redox equation involving two soluble species, the curves shown are for fixed values of the log of the product concentration over the reactant concentration. For instance Figure 3, reaction 1, shows curves for log ($\{Fe^{2+}\}/\{Fe^{3+}\}$) equal to 10, 5, and 0 (equal amounts of each). In the region where pE is less than 3, the prevalence of Fe^{2+} is so dominant that all iron could be considered Fe^{2+} and redox reaction 1 and Fe^{3+} could be ignored. When reactions involve one mole of product and one mole of reactant, the curves do not depend on total concentrations. However, when unequal amounts of product and reactant are involved, then curves also depend on total concentration. An example of this is shown by reaction 4. The total concentrations shown are the sums of the activities of free mercury (I) and free mercury (II). They do not necessarily represent total dissolved mercury. In this figure, the curve labeled 15b represents the pE and pH conditions at which log ($\{Hg_2^{2+}\}/\{Hg^{2+}\}$) = 15 and $\{Hg^{2+}\} + 2\{Hg_2^{2+}\} = 10^{-5}M$.

The representations for solids differ slightly. As solubility decreases, the concentrations of reacting species become necessarily smaller. The curves show under what pE and pH conditions a particular activity (usually 10^{-5}, 10^{-10}, $10^{-15}M$) of the reacting species would be in equilibrium with solid. When the maximum free concentration of the reacting species is very small, much of that species is considered to be in the solid form. For example, in reaction 2 at pH 8 and pE 12 most Mn^{2+} would be oxidized to $MnO_2(s)$.

In using these diagrams it is well to remember that one is dealing with multiple simultaneous reactions. Precipitation of solids and formation of complexes may lead to a large total concentration of a species in a given oxidation state even though the free concentration of that state may be smaller than the free concentration of a different oxidation state.

Computations using redox reactions lead to many errors in running the REDEQL program. Those reactions in which the curves are close together on the pE - pH diagrams (e.g. reactions 8 and 9) are the most difficult to use because numbers which are too small or too large for the computer to handle can easily be generated during computation. This causes the program to fail.

VII. SATURATION RATIOS

A chemist or geologist is often interested in whether a solution is supersatured or undersaturated with respect to a particular solid phase. REDEQL.EPAK will determine this for any solids specified, even if imposed or disallowed. The number of solids to be checked (up to 13) is given in field 18 of the program header card (see Table 1). The solids to be checked, identified by metal and ligand reference numbers and 1, 2, or 3 for their position in the thermodynamic data base, are given on card type 10a which precedes the card listing redox reactions in the input data deck (see Table 1). Only one solid of a given metal and ligand may be checked. The logs of the ratio of ion products to the solubility products are given by an output routine called immediately after the case progress output routine.

VIII. ADSORPTION

The adsorption routine available with REDEQL.EPAK is a surface complexation adsorption model. The prototype of this model was described in a draft of the California Institute of Technology Technical Report EQ-76-01 by McDuff and Morgan[17]. Their work was patterned after that of Schindler et al.[18], Hohl and Stumm[19], and Vuceta[20]. Only "ligand" surfaces are considered. There are no thermodynamic data on file; data must be provided by the user. The constants given here are for the sake of example only. Experimentally determined adsorption constants depend heavily upon the hydrolysis constants of the adsorbing metals. The user should ensure that hydrolysis constants in the thermodynamic data base are consistent with those that were used to determine adsorption constants. Numerous adsorption models are currently in use by various researchers. Their abundancy is a reflection on their general inadequacy, and the model used here is no exception.

The model allows one to consider five surfaces at one time. Any number of metals and hydrolyzed metals may adsorb on any or all of the surfaces. This model does not include adsorption of ligands or metal-ligand complexes.

For each surface one must know the pH at which it carries no charge (pH_{ZPC}) and the constants for association with, or loss of, hydrogen ions. Surface concentrations of hydrogen exchange sites or surface complexes are given in moles of the species on surfaces in one liter of solution and will be denoted { }, while molar concentrations are denoted [ ]. Every surface HS can gain or lose H^+:

$$H_2S^+ \rightarrow H^+ + HS \qquad K^s_{a_1,app}$$

$$HS \rightarrow H^+ + S^- \qquad K^s_{a_2,app}$$

so

$$\{S^-\} = K^s_{a_2,app}\ \{HS\}\ [H^+]^{-1}$$

and

$$\{H_2S^+\} = (K^s_{a_1,app})^{-1}\ \{HS\}\ [H^+]$$

The constants are apparent constants because they depend on the local electric field at the surface which, in this work is considered to be a function only of pH due to a Nernstian surface potential. Validity of this type of poten-

tial generally is limited to a narrow pH range about pH_{ZPC}. The apparent constants may be related to intrinsic constants by

$$K^s_{a_i,app} = K^s_{a_i,intr}\ 10^{\alpha(pH_{ZPC} - pH)}$$

The constant α is a scaling parameter (0 1) for the influence of the surface potential. The intrinsic constants are required by the program.

For metal adsorption or exchange of the types

$$M^{+z} + HS - H^+ \rightarrow MS^{z-1} \qquad {}^*K^s_{1,app}$$

and

$$M^{+z} + 2HS - 2H^+ \rightarrow MS_2{}^{z-2} \qquad {}^*\beta^s_{2,app}$$

the amounts of surface complexes formed are

$$\{MS^{z-1}\} = {}^*K^s_{1,app}\ \{HS\}\ [M^{z+}][H^+]^{-1}$$

and

$$\{MS_2{}^{z-2}\} = {}^*\beta^s_{2,app}\ \{HS\}^2[M^{z+}][H^+]^{-2}$$

The apparent constants are related to the intrinsic constants by

$${}^*K^s_{1,app} = {}^*K^s_{1,intr}\ 10^{(z-1)\alpha(pH - pH_{ZPC})}$$

$${}^*\beta^s_{2,app} = {}^*\beta^s_{2,intr}\ 10^{(z-2)\alpha(pH - pH_{ZPC})}$$

This theory assumes that surface potential is not affected by adsorption of metal ions, which is a good assumption only when a small fraction of the surface sites are used in adsorption.

Because of the form of these equations the complexes between surfaces and adsorbing metals can be treated just as other complexes in the program. The intrinsic constant is corrected to an apparent constant every time pH is modified during program execution. The constants (intrinsic and apparent) are

very dependent on the ionic strength and also ionic medium and must be measured for each medium. These constants are not corrected within the program for changes in ionic strength.

As a brief example of typical data, Schindler et al.[18] found that for adsorption of Cu (II) on α-quartz (pH_{ZPC} = 2.0), log ${}^{*}K_1^s \cong$ -8.3 and log ${}^{*}\beta_2^s \cong$ -17.6 in 1M $NaClO_4$. These were apparent constants but appeared to be independent of pH so ${}^{*}K_1^s = {}^{*}K_{1,intr}^s$ and α = 0.0. Schindler and Kamber[21] found that log $K_{a_2,intr}^s$ = -6.8. This constant however will definitely vary with pH and to use the constant α = 0, the user would probably want to calculate $K_{a_2,app}^s$ for each pH considered from the expression given above or from empirical expressions given by authors, e.g. from Schindler et al.[18], when (SiOH) = 1.45 total moles/kg

$$\log (SiO^-) = \frac{\log (-\log [H^+])}{0.1923} - 5.349$$

where (SiO^-) is the surface concentration in moles per kg.

The formats for adsorption input data are shown in Table 1 (Table 4p). The number of ligand surfaces is indicated in field 6 (column 18) of the program header card (1). The data cards are required for each ligand surface. The first surface card (type 4a) follows the ligand input and contains the surface concentration of the surface as moles of adsorbing sites per liter of solution (calculated from surface sites/kg and kg/l) for each case as well as an initial guess as to free surface sites and a reference number (90-95) for the ligand. The other adsorption cards are placed at the end of the deck. There is one card of type (13) for each surface. It contains pH_{ZPC}, the intrinsic constant for loss of H^+, the intrinsic constant for gain of H^+ if given, α, and the number of metals which can complex with the ligand. Each metal requires a card of type (14) following the ligand surface card (13). The metal cards give the reference number of the metal, the number of complexes formed, and the intrinsic constant and stiochiometry (metal, ligand, and H^+) for each complex.

IX. INTERNAL CHANGES IN THE REDEQL PROGRAM

In addition to the functional changes mentioned in this report, the FORTRAN version of the program has been rewritten. As a first step, the variables used in many subroutines were regrouped into new blocks of common in an attempt to clarify which variables were used in each subroutine and to decrease the number of lines of common at the beginning of each subroutine.

Code was changed so that metals and ligands are treated more similarly, often by using subroutines called first for metals then for ligands. Repetitive activity coefficient computations were eliminated. A new internal system of indexing complexes and solids was designed so that many large arrays, (20,30,6) and (20,30,3), were replaced by smaller arrays, (750) and (100).

The FORTRAN version of the program which now contains many comment cards is available upon request or can be listed from COMNET by logging on to WCC and using the following command

PRINT CN.EPABDJ.CPR1.REDEQL.EPAK,ROUTE=REMOTENN

where NN is the user's terminal number.

For those wishing to modify the program, expand it, or to understand it, this guide includes a flow diagram of the program subroutines. Appendix B shows all of the subroutines in REDEQL.EPAK. Every subroutine is called unless a diamond-shaped decision box is shown. Areas enclosed in dashed-line boxes involve operations of a single subroutine. Routines SUB1, SUB2, and SUB3 control the calling of almost all other subroutines and their calls and decisions are shown in a column and are not enclosed in dashed-lines for simplicity. Utility subroutines called at different points in the flow are shown each time they are called. An explanation of the purpose of the subroutine is shown to the side of the flow diagram the first time the subroutine is called. Subroutines called repeatedly at one point in the program flow are shown only once. Subroutines which involve input or output are shown as parallelograms.

The program was written for an IBM compiler and much of the program is language dependent. If the user wishes to adapt the program to another computer system the following problems may be encountered. Suggested solutions and time estimates are given below.

1) Problem: The program uses four types of variables:

INTEGER*2	2 Bytes (1 Byte = 8 bits)
INTEGER	4 Bytes
REAL	4 Bytes
REAL*8	8 Bytes

The INTEGER*2 declaration is used for arrays of integer values to save memory. Arrays of 8-character names (i.e. NAMEM and NAMER) are declared REAL *8.

Solution: Change all INTEGER*2 and REAL*8 declarations to integer. (Trivial)

2) Problem: The main program has no program statement.

Solution: Add the program statement.
TAPE5 = User Data Deck
TAPE10 = Thermodynamic Data File
TAPE6 = Printout
(Trivial)

3) Problem: Values in common arrays must be initialized in BLOCK DATA modules. The module in REDEQL.EPAK that zeroes out the common blocks assumes that certain arrays are INTEGER*2.

Solution: A) If BLOCK DATA is allowed, rewrite the first BLOCK DATA module using recomputed common block lengths. (2 hr).

B) If block data is disallowed, move the text of the BLOCK DATA modules to the main program. (Trivial)

C) If the system automatically initializes common blocks to zero, delete the first module. (Trivial)

4) Problem: Common statements in different subroutines may imply different lengths for the same common block.

Solution: Use the complete common statement each time a block is declared. (1 Day).

5) Problem: Subscript expressions are not limited to the standard forms.

Solution: Rewrite statements that use unacceptable subscript expressions. (3 Days)

6) Problem: To save source code, many arithmetic expressions mix real and integer (or INTEGER*2) variables without the benefit of FLOAT and IFIX functions.

Solution: A) Leave mixed-mode expressions for the compiler to handle. (Trivial)

B) Add calls to FLOAT and IFIX where they are appropriate. (5 days)

C) Change variable type from INTEGER(*2) to REAL where it is appropriate. (8 days)

7) Problem: Subroutine IONCR uses a statement function, GAM.

Solution: Rewrite GAM as a function subroutine. (Trivial)

8) Problem: Several subroutines use multiple returns to replace IF statements in the calling routines.

Solution: Set flags in the called routines and check them in the calling routines. (1 Day)

9) Problem: Some format statements use the P scale factor.

Solution: Input -- Omit scale factors and perform the implied scaling after the appropriate read statements. (4 Hr.)

Output -- Omit scale factors. (2 hr.)

10) Problem: Subroutine ERRSET, called by the main program, is an IBM system routine.

Solution: Delete the call to errset. (Trivial)

11) Problem: Certain parameters in the subroutine statements are enclosed in slashes (i.e. /T/ in DEFALT, /MI/ in INCONC, and /CSTOIC/ in OUT141).

Solution: Delete the slashes. (Trivial)

REFERENCES

1. Kjaraka, Y. K. and I. Barnes. SOLMNEQ: Solution-Mineral Equilibrium Computations, NTIS Tech. Rept. PB214-899, Springfield, VA. 82 p. (1973).

2. Mattigod, S. V. and G. Sposito. Chemical Modeling of Trace Metal Equilibria in Contaminated Soil Solutions Using the Computer Program GEOCHEM, Jenne, E. A., ed., in Chemical Modeling in Aqeous Systems. Speciation, Sorption, Solubility, and Kinetics. Amer. Chem. Soc., Symposium Series 93. Wash. D.C. 914 p. (1979).

3. Plummer, L. N., B. F. Jones, and A. H. Truesdell. WATEQF--a FORTRAN IV Version of WATEQ, a Computer Program for Calculating Chemical Equilibrium of Natural Waters, U.S. Geol. Survey Water Resour. Invest. 76-13. 61 p. (1976).

4. Truesdell, A. H. and B. F. Jones. WATEQ, a Computer Program for Calculating Chemical Equilibria of Natural Waters, J. Res. U.S. Geol. Survey 2, 233-274 (1974).

5. Westall, J. C., J. L. Zachary, and F. M. M. Morel. MINEQL, a Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems, Tech. Note 18, Dept. Civil Eng. Mass. Inst. Tech., Cambridge, MA. 91 p. (1976).

6. Wigley, T. M. L. WATSPEC: a Computer Program for Determining the Equilibrium Speciation of Aqueous Solutions, Brit. Geomorph. Res. Group Tech. Bull. 20. 48 p. (1977).

7. McDuff, R. E. and F. M. Morel. Description and Use of the Chemical Equilibrium Program REDEQL2, Keck Lab. Tech. Rept. EQ-73-02, Calif. Inst. Tech., Pasadena, CA. 75 p. (1973).

8. McCrady, J. K., and G. A. Chapman. Determinations of Copper Complexing Capacity of Natural River Water, Well Water and Artificially Reconstituted Water. Water Research 13:143-150 (1979).

9. Volk, B. G., and B. Lighthart. Computed Equilibrium Speciation of Cadmium in Soil Solutions of Varying Organic Content, pH, and CO_2 Concentration. International Soc. of Soil Science, 11th Congress, Abstract for Commission Papers. Vol 1. p. 292, Edmonton, Canada. (1978).

10. Morel, F. M. M., J. C. Westall, C. R. O'Melia and J. J. Morgan. Fate of Trace Metals in Los Angeles County Wastewater Discharge. Environ. Sci. Tech., 9:756-761 (1975).

11. Theis, T. L. and R. O. Richter. Chemical Speciation of Heavy Metals in Power Plant Ash Pond Leachate. Environ. Sci. Tech., 13:219-224 (1979).

12. Magnuson, V. R., D. K. Harriss, M. S. Sun, D. K. Taylor and G. E. Glass. Relationship of Activities of Metal-Ligand Species to Aquatic Toxicity, Jenne, E. A., ed., in Chemical Modeling in Aqueous Systems. Speciation, Sorption, Solubility and Kinetics. Amer. Chem. Soc. Symposium Series 93, Wash. D.C. 914 p. (1979).

13. Ingle, S. E., M. D. Schuldt, and D. W. Schults. A User's Guide to REDEQL.EPA, A Computer Program for Chemical Equilibria in Aqueous Systems, USEPA Corvallis Environmental Research Laboratory, EPA-600/3-78-024, NTIS PB 280 149/6BE, Corvallis, OR (1978).

14. Smith, R., and A. Martell. Critical Stability Constants, Vol 1 (1974), Vol. 2 (1975), Vol. 3 (1977), Vol. 4 (1976), Plenum Press, New York.

15. Morel, F., and J. J. Morgan. A Numerical Method for Computing Equilibrium in Aqueous Chemical Systems. Environ. Sci. Tech., 6:58-67 (1972).

16. Malmberg, C. G., and A. A. Maryott. Dielectric Constant of Water from 0° to 100°C. J. Res. Nat. Bur. Stds., 56, 1-8 (1956).

17. McDuff, R. E., and J. J. Morgan. Adsorption of Metal Ions as Surface Complex Formation (How REDEQL Absorps the "Swiss" Adsorption). Keck Laboratories, Calif. Inst. Tech., Pasadena, CA (1976).

18. Schindler, P. W., B. Fürst, R. Dick, and P. U. Wolf. Ligand Properties of Surface Silanol Groups. J. Colloid Interface Sci., 55, 469-475 (1976).

19. Hohl, H., and W. Stumm. Interaction of Pb^{2+} with Hydrous γ - Al_2O_3. J. Colloid Interface Sci., 55, 231 (1976).

20. Vuceta, J. Adsorption of Pb (II) and Cu (II) on α-Quartz from Aqueous Solution: Influence of pH, Ionic Strength and Complexing Ligands. Ph.D. Thesis, Calif. Inst. Tech., Pasadena, CA (1976).

21. Schindler, P., and H. R. Kamber. The Acidity of Silanol groups. Helvetica Chimica Acta, 51, 1781-1786 (1968).

Table 1. Changes to Tables in Previous User's Guide**

Table 1p. Reference Numbers for Metals and Ligands

Metal 35 = Hg_2^{2+}

Ligand 59 = CrO_4^{2-}

Table 2p. Redox Reactions

Reference Number	Reaction Type	Reaction	Log K
4	-10	$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ (aq)	30.7
16	DELETE		
17	DELETE		
18	-11	$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^-$	-74.9

Table 4p. Program Input Cards

Card Type	Card Field	Columns	Description
(1) Program Header Card: 1 card, Format (18I3,1X,F4.1,2I3). All blanks are read as zeros.			
	1-5		As described previously
	6	17-18	Number of adsorbing ligand surfaces
	7-17		As described previously
	18	53-54	Selects degree of saturation output routine. 0 means none will be checked. N, where 0<N≤13, means that the degree of saturation will be checked for N solids.
	19	56-59	Celsius temperature other than 25. Zero reads as 25°C, i.e. no temperature corrections.

** Ingle, S.E., M. D. Schuldt, and D. W. Schults. A User's Guide to REDEQL.EPA, A Computer Program for Chemical Equilibrium in Aqueous Systems. USEPA Corvallis Environmental Research Laboratory, EPA-600/3-78-024. Corvallis, Oregon, 1978.

Preceding page blank

Table 1. (Continued)

20	60-62	Reference number of ligand to be adjusted for charge balance if pH is fixed. 0 if all adjusted 100 if none adjusted
21	64-65	Normal charge of ligand in field 20 including sign.

(4a) Adsorbing surface concentration cards, # cards = # given in field 6, column 18 of the program header card, Format (I2,2X,11(1X,F5.2)).

1	1-2	Reference number assigned to the surface. (90-95)
2	6-10	Guess for moles of unreacted surface sites on surfaces in one liter of solution.
3	12-16	Total moles of exchange sites on surface in one liter of solution for first case.
4	18-22	Total moles of exchange sites per liter of solution for second case.
5	24-28	Etc.
6-12		

(6) OMIT TOTH CARD NEVER NEEDED

(10a) (Follows 10, before 11)

Saturation card: 1 card used only if the degree of saturation of one or more solids is to be checked (field 18 of the program header card > 0). Format 39I2.

1	1-2	Reference number of metal in Solid A.
2	3-4	Reference number of ligand in Solid A.
3	5-6	1, 2, or 3 depending on whether A is the first, second or third solid listed in the thermodynamic data file.
4	7-8	Reference number of metal in Solid B.
Etc.		As in card 10.

Table 1. (Continued)

(13) Adsorbing surface cards, # cards = # given in field 6, column 18 of the program header card, Format (3F5.2,2I5,F5.2).

1	1-5	pH_{ZPC} for adsorbing surface
2	6-10	$-\log {}^{*}K^{s}_{a_2}$, intrinsic
3	11-15	$-\log {}^{*}K^{s}_{a_1}$, intrinsic
4	20	1, if a value given in field 3. 0, if no value given in field 3.
5	24-25	Number of metals which will complex with the surface.
6	28-30	Alpha, (1.0 - 0.0).

(14) Metal adsorption cards: # cards = # given in field 5 of preceding surface card (13), Format (2I5,3(F5.0,3I5)).

1	4-5	Reference number of the metal.
2	10	Number of complexes to follow ($\leq$ 3).
3	11-15	100 x log of intrinsic formation constant for the first complex.
4	19-20	Stoichiometric coefficient of metal in the first complex.
5	24-25	Stoichiometric coefficient of the ligand surface in the first complex.
6	29-30	Stoichiometric coefficient of hydrogen (hydroxide if negative) in the first complex.
7	31-35	100 x log of intrinsic formation constant for the second complex.
8	9-40	Stoichiometric coefficient of metal in the second complex.
9-14		Etc.

Table 1. (Continued)

Table 6p. Thermodynamic Data Deck

Card Type	Card Field	Columns	Description
(4)	Solid and complex header card: 1 card, Format (I5,F5.2,F5.1,F6.2,F5.2).		
	1-3		As described previously
	4	16-21	ΔH for the dissociation of water in Kcal/mole.
	5	22-27	10 X ΔH for the reaction $2H^+ + CO_3^{2-} \rightarrow CO_2(g) + H_2O$ in Kcal/mole.
(5)	Solid and complex cards: # cards = # given on header card (4), Format 2I2,9(I4,2I1,I2),2X,I1.		
	1-38		As described previously
	39	79	0 if no enthalpy card (5a) follows. 1 if enthalpy card (5a) follows.
(5a)	(One card follows each card of type (5) which contains 1 in column 79.) Solid and complex enthalpy data cards: Format (2I3,9(4X,F4.0)).		
	1	1-2	Reference number of metal
	2	3-4	Reference number of ligand
	3	9-12	10 x enthalpy of formation of the first solid listed on the preceeding type (5) card.
	4	17-20	10 x enthalpy of formation of the second solid.
	5	25-28	10 x enthalpy of formation of the third solid.
	6	33-36	10 x enthalpy of formation of the first complex.
	Etc.		Enthalpies for remaining five complexes.
(7)	Redox reaction cards: # cards = # given on header card (6), Format (9I5,A8,F4.0)		
	2	9-10	Reference # of reacting metal (if type -11).

Table 1. (Continued)

3	14-15	Reference # of ligand produced (if type -11).
4	18-20	Reaction type -11 metal to ligand redox, as well as those reaction types given previously.
8	39-40	Stoichiometric coefficient of ion given in field 2.
11	54-57	10 x enthalpy of formation

(9) Mixed solids cards: # cards = # given on header card (8), Format (11I4,I6, 2I3,A8,2F7.2)

1-16		As described previously.
17	72-78	10 x enthalpy of reaction

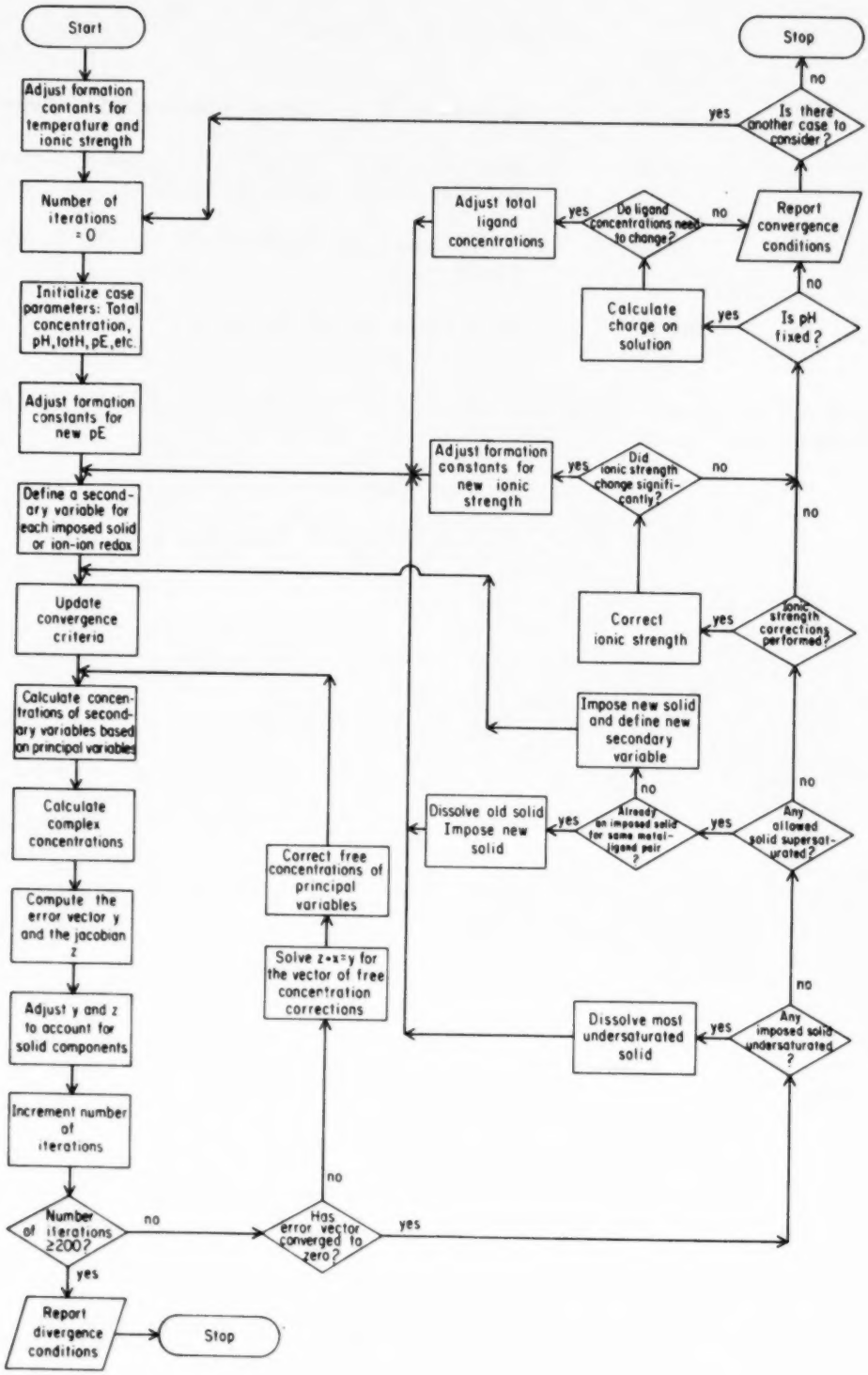


Figure 1. Flow diagram for REDEQL.EPAK

Figure 2. An example with two cases.

2a. Input data.

2a(i). The raw data.

Data	Where, Field
10 metals (shown below + H^+)	Card 1, field 1
10 ligands (shown below +OH^-)	Card 1, field 2
2 cases	Card 1, field 3
No solids initially present	Card 1, field 4
No adsorption	Card 1, field 5+6
Fixed pH	Card 1, field 7
8.0 (both cases)	Card 5
No redox, no mixed solids	Card 1, fields 8, 9
Ionic strength to be calculated	Card 1, field 10
Guess 0.1	Card 2
Normal outputs	Card 1, fields 11-17
Check saturation of 2 solids	Card 1, field 18
$CaCO_3$, $MgCO_3$	Card 10a
Temperature, 20.0°C	Card 1, field 19
Adjust ligands for charge balance	Card 1, field 20

Card 3

Field 1		Field 3	
Metals	Ref.	M	-log M
Ca^{2+}	1	7.4×10^{-5}	4.15
Mg^{2+}	2	4.6×10^{-5}	4.34
K^+	4	2.3×10^{-5}	4.64
Na^+	5	5.2×10^{-4}	3.28
Fe^{3+}	6	2.0×10^{-8}	7.70
Fe^{2+}	7	4.3×10^{-7}	6.37
Cu^{2+}	9	1.2×10^{-7}	6.93
Zn^{2+}	12	2.5×10^{-7}	6.61
Cr^{3+}	19	2.2×10^{-7}	6.66

Card 4

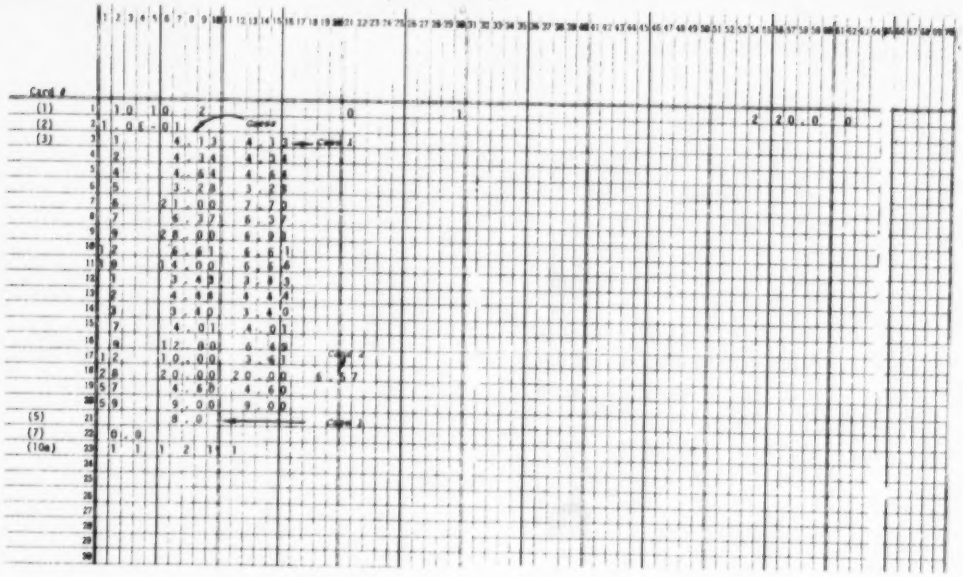
Field 1			Field 3
Metals	Ref.	M	-log M
CO_3^{2-}	1	3.7×10^{-4}	3.43
SO_4^{2-}	2	3.6×10^{-5}	4.44
Cl^-	3	4.0×10^{-4}	3.40
NH_3	7	9.8×10^{-5}	4.01
PO_4^{3-}	9	3.2×10^{-7}	6.49
SiO_3^{2-}	12	2.5×10^{-4}	3.61
$EDTA^{4-}$	28	1.0×10^{-20}	20.00
		(2.7×10^{-7}	(6.57)
NO_3^-	57	2.5×10^{-5}	4.60
CrO_4^-	59	1.0×10^{-9}	9.00

Card 7

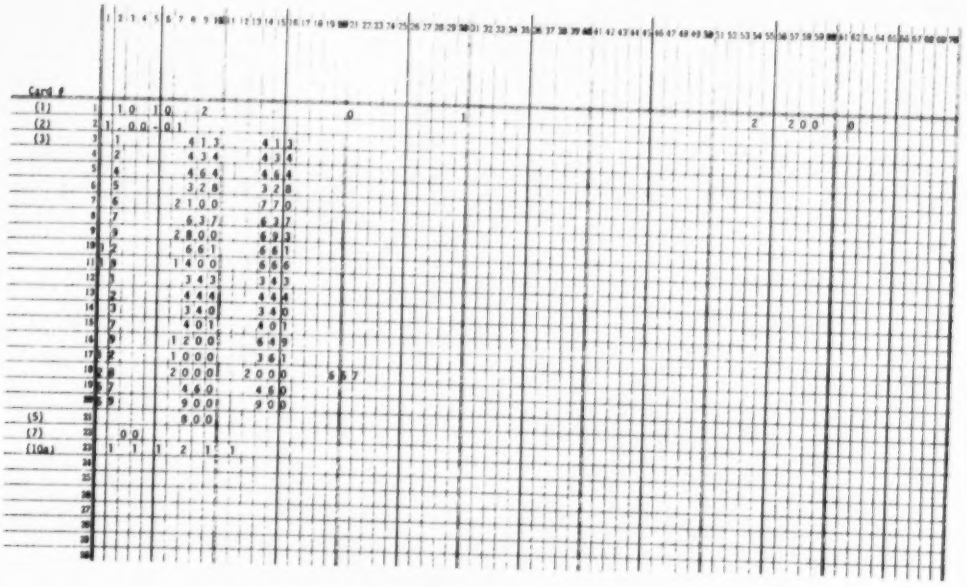
Partial Pressure CO_2 = 0.0

Figure 2. (continued)

2a(ii). One form of the input data.



2a(iii). The input data employing input data sheets.



Reproduced from
best available copy.

INPUT DATA FOR VERIFICATION

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH OF 0.999999[illegible]E-01 AND A TEMPERATURE OF 20.0 DEGREES CELSIUS

MET	LIG	• SOLIDS 1				2				3				• COMPLEXES 1				2				3				4				5				6			
M	CO3-	14	0	1	2	0	0	0	0	0	0	0	0	1036	0	1	1	1414	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M	SO4	0	0	0	0	0	0	0	0	0	0	0	0	154	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M	CL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M	NH3	0	0	0	0	0	0	0	0	0	0	0	0	941	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M	PO4	0	0	0	0	0	0	0	0	0	0	0	0	1182	0	1	1	1913	0	1	2	2082	0	1	3	0	0	0	0	0	0	0	0	0	0	0	0
M	SIO3	2514	0	1	2	0	0	0	0	0	0	0	0	1270	0	1	1	2[illegible]	0	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	1046	0	1	1	1704	0	1	2	1475	0	1	3	2178	0	1	4	0	0	0	0	0	0	0	0
M	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	610	0	1	1	574	0	1	2	1404	0	2	2	1365	0	2	3	0	0	0	0	0	0	0	0
M	OH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	CO3-	750	1	1	0	0	0	0	0	0	0	0	0	230	1	1	0	1046	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	SO4	371	1	1	0	0	0	0	0	0	0	0	0	134	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	CL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	NH3	0	0	0	0	0	0	0	0	0	0	0	0	-10	1	1	0	-30	1	2	0	-150	1	3	0	-259	1	4	0	0	0	0	0	0	0	0	0
Ca	PO4	3490	5	1	-1	4334	4	1	1	1749	1	1	1	1359	1	1	1	515	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	SIO3	630	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	1041	1	1	0	1372	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	OH	-2341	1	0	-2	0	0	0	0	0	0	0	0	-1297	1	0	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	CO3-	660	1	1	0	0	0	0	0	0	0	0	0	200	1	1	0	1046	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	SO4	0	0	0	0	0	0	0	0	0	0	0	0	128	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	CL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	NH3	0	0	0	0	0	0	0	0	0	0	0	0	11	1	1	0	20	1	2	0	-30	1	3	0	-100	1	4	0	0	0	0	0	0	0	0	0
Mg	PO4	2504	3	2	0	0	0	0	0	0	0	0	0	1379	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	SIO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	731	1	1	0	1142	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mg	OH	-1723	1	0	-2	0	0	0	0	0	0	0	0	-1167	1	0	-1	-3977	1	0	-4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	CO3-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	SO4	0	0	0	0	0	0	0	0	0	0	0	0	45	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	CL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	NH3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	PO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	SIO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K	OH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	CO3-	0	0	0	0	0	0	0	0	0	0	0	0	75	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	SO4	0	0	0	0	0	0	0	0	0	0	0	0	23	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	CL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	NH3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	PO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	SIO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	140	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na	OH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	CO3-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	SO4	0	0	0	0	0	0	0	0	0	0	0	0	265	1	1	0	341	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	CL	0	0	0	0	0	0	0	0	0	0	0	0	75	1	1	0	98	1	2	0	-4	1	3	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	NH3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	PO4	2434	1	1	0	0	0	0	0	0	0	0	0	1874	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	SIO3	0	0	0	0	0	0	0	0	0	0	0	0	2243	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	2611	1	1	0	2765	1	1	1	1870	1	1	-1	922	1	1	-2	0	0	0	0	0	0	0	0
Fe3	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe3	OH	-4[illegible]01	1	0	-3	0	0	0	0	0	0	0	0	-270	1	0	-1	-648	1	0	-2	-2227	1	0	-4	-301	2	0	-2	0	0	0	0	0	0	0	0
Fe2	CO3-	980	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	SO4	0	0	0	0	0	0	0	0	0	0	0	0	130	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	CL	0	0	0	0	0	0	0	0	0	0	0	0	45	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	NH3	0	0	0	0	0	0	0	0	0	0	0	0	130	1	1	0	210	1	2	0	359	1	4	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	PO4	3264	3	2	0	0	0	0	0	0	0	0	0	1449	1	1	1	2084	1	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	SIO3	1550	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	1491	1	1	0	1792	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe2	OH	-1323	1	0	-2	0	0	0	0	0	0	0	0	-977	1	0	-1	-3216	1	0	-3	-4617	1	0	-4	0	0	0	0	0	0	0	0	0	0	0	0
Cu	CO3-	477	2	1	-2	870	1	1	0	0	0	0	0	590	1	1	0	980	1	2	0	1166	1	1	1	-1333	1	1	-2	0	0	0	0	0	0	0	0
Cu	SO4	0	0	0	0	0	0	0	0	0	0	0	0	148	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu	CL	0	0	0	0	0	0	0	0	0	0	0	0	-4	1	1	0	152	1	2	0	122	1	3	0	95	1	4	0	-540	1	1	-1	0	0	0	0
Cu	NH3	0	0	0	0	0	0	0	0	0	0	0	0	309	1	1	0	749	1	2	0	1029	1	3	0	1179	1	4	0	0	0	0	0	0	0	0	0
Cu	PO4	3434	3	2	0	0	0	0	0	0	0	0	0	1449	1	1	1	1984	1	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu	SIO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	1941	1	1	0	2262	1	1	1	792	1	1	-1	0	0	0	0	0	0	0	0	0	0	0	0
Cu	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu	CRO4	450	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu	OH	-903	1	0	-2	0	0	0	0	0	0	0	0	-797	1	0	-1	-1763	1	0	-2	-2696	1	0	-3	-3937	1	0	-4	-1063	2	0	-2	0	0	0	0
Zn	CO3-	910	1	1	0	0	0	0	0	0	0	0	0	440	1	1	0	1136	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	SO4	0	0	0	0	0	0	0	0	0	0	0	0	148	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	CL	0	0	0	0	0	0	0	0	0	0	0	0	-4	1	1	0	102	1	2	0	-17	1	3	0	-750	1	1	-1	-24	1	4	0	0	0	0	0
Zn	NH3	0	0	0	0	0	0	0	0	0	0	0	0	220	1	1	0	449	1	2	0	689	1	3	0	849	1	4	0	0	0	0	0	0	0	0	0
Zn	PO4	3194	3	2	0	0	0	0	0	0	0	0	0	1369	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	SIO3	1760	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	1721	1	1	0	2042	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	OH	-1283	1	0	-2	0	0	0	0	0	0	0	0	-927	1	0	-1	-2856	1	0	-3	-4097	1	0	-4	-1723	1	0	-2	-883	2	0	-1	0	0	0	0
Cd	CO3-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	SO4	0	0	0	0	0	0	0	0	0	0	0	0	135	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	CL	0	0	0	0	0	0	0	0	0	0	0	0	12	1	1	0	-111	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	NH3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	PO4	0	0	0	0	0	0	0	0	0	0	0	0	1954	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	SIO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	EDTA	0	0	0	0	0	0	0	0	0	0	0	0	2411	1	1	0	2635	1	1	1	1670	1	1	-1	0	0	0	0	0	0	0	0	0	0	0	0
Cd	NO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	CRO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cd	OH	-1283	1	0	-3	0	0	0	0	0	0	0	0	-455	1	0	-1	-958	1	0	-2	-2447	1	0	-4	0	0	0	0	0	0	0	0	0	0	0	0

Figure 2b. Thermodynamic data at 20°C, 0.1 ionic strength

THERMODYNAMIC CONSTANTS CORRECTED TO IONIC STRENGTH OF 0.9999999E-01 AND A TEMPERATURE OF 25.0 DEGREES CELSIUS

MET	LIG	SOLIDS 1		SOLIDS 2		SOLIDS 3		COMPLEXES 1		COMPLEXES 2		COMPLEXES 3		COMPLEXES 4		COMPLEXES 5		COMPLEXES 6	
H	CO3-	11	0 1 2	0	0 0 0	0	0 0 0	990	0 1 1	1613	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
H	SO4	0	0 0 0	0	0 0 0	0	0 0 0	160	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
H	CL	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
H	NH3	0	0 0 0	0	0 0 0	0	0 0 0	925	0 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
H	PO4	0	0 0 0	0	0 0 0	0	0 0 0	1178	0 1 1	1858	0 1 2	2051	0 1 3	0	0 0 0	0	0 0 0	0	0 0 0
H	SIO3	2511	0 1 2	0	0 0 0	0	0 0 0	1270	0 1 1	2241	0 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
H	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	1045	0 1 1	1703	0 1 2	1974	0 1 3	2177	0 1 4	0	0 0 0	0	0 0 0
H	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
H	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	610	0 1 1	573	0 1 2	1403	0 2 2	1364	0 2 3	0	0 0 0	0	0 0 0
H	OH	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	CO3-	749	1 1 0	0	0 0 0	0	0 0 0	229	1 1 0	1045	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	SO4	369	1 1 0	0	0 0 0	0	0 0 0	139	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	CL	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	NH3	0	0 0 0	0	0 0 0	0	0 0 0	-10	1 1 0	-70	1 2 0	-150	1 3 0	-259	1 4 0	0	0 0 0	0	0 0 0
CA	PO4	3985	5 3-1	4324	4 3 1	1767	1 1 1	1357	1 1 1	514	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	SIO3	829	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	1079	1 1 0	1370	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CA	OH	-2313	1 0-2	0	0 0 0	0	0 0 0	-1298	1 0-1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	CO3-	659	1 1 0	0	0 0 0	0	0 0 0	199	1 1 0	1045	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	SO4	0	0 0 0	0	0 0 0	0	0 0 0	129	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	CL	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	NH3	0	0 0 0	0	0 0 0	0	0 0 0	10	1 1 0	20	1 2 0	-30	1 3 0	-100	1 4 0	0	0 0 0	0	0 0 0
MG	PO4	2501	3 2 0	0	0 0 0	0	0 0 0	1377	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	SIO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	729	1 1 0	1160	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
MG	OH	-1723	1 0-2	0	0 0 0	0	0 0 0	-1168	1 0-1	-3977	4 0-4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	CO3-	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	SO4	0	0 0 0	0	0 0 0	0	0 0 0	44	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	CL	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	NH3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	PO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	SIO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
K	OH	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	CO3-	0	0 0 0	0	0 0 0	0	0 0 0	74	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	SO4	0	0 0 0	0	0 0 0	0	0 0 0	24	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	CL	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	NH3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	PO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	SIO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	184	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
NA	OH	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	CO3-	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	SO4	0	0 0 0	0	0 0 0	0	0 0 0	264	1 1 0	359	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	CL	0	0 0 0	0	0 0 0	0	0 0 0	82	1 1 0	97	1 2 0	-5	1 3 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	NH3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	PO4	2437	1 1 0	0	0 0 0	0	0 0 0	1872	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	SIO3	0	0 0 0	0	0 0 0	0	0 0 0	2242	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	2609	1 1 0	2762	1 1 1	1868	1 1-1	920	1 1-2	0	0 0 0	0	0 0 0
FE3	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE3	OH	-404	1 0-3	0	0 0 0	0	0 0 0	-270	1 0-1	-648	1 0-2	-2227	1 0-4	-301	2 0-2	0	0 0 0	0	0 0 0
FE2	CO3-	979	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	SO4	0	0 0 0	0	0 0 0	0	0 0 0	129	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	CL	0	0 0 0	0	0 0 0	0	0 0 0	44	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	NH3	0	0 0 0	0	0 0 0	0	0 0 0	130	1 1 0	210	1 2 0	359	1 4 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	PO4	3291	3 2 0	0	0 0 0	0	0 0 0	1447	1 1 1	2083	1 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	SIO3	1549	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	1489	1 1 0	1790	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
FE2	OH	-1323	1 0-2	0	0 0 0	0	0 0 0	-978	1 0-1	-3216	1 0-3	-4517	1 0-4	0	0 0 0	0	0 0 0	0	0 0 0
CU	CO3-	476	2 1-2	869	1 1 0	0	0 0 0	589	1 1 0	899	1 2 0	1165	1 1 1	-1333	1 1-2	0	0 0 0	0	0 0 0
CU	SO4	0	0 0 0	0	0 0 0	0	0 0 0	149	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CU	CL	0	0 0 0	0	0 0 0	0	0 0 0	-5	1 1 0	152	1 2 0	122	1 3 0	94	1 4 0	-540	1 1-1	0	0 0 0
CU	NH3	0	0 0 0	0	0 0 0	0	0 0 0	399	1 1 0	749	1 2 0	1029	1 3 0	1179	1 4 0	0	0 0 0	0	0 0 0
CU	PO4	3431	3 2 0	0	0 0 0	0	0 0 0	1447	1 1 1	1983	1 1 2	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CU	SIO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CU	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	1939	1 1 0	2260	1 1 1	791	1 1-1	0	0 0 0	0	0 0 0	0	0 0 0
CU	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CU	CRO4	449	1 1 0	0	0 0 0	0	0 0 0	0	0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CU	OH	-903	1 0-2	0	0 0 0	0	0 0 0	-798	1 0-1	-1763	1 0-2	-2696	1 0-3	-3937	1 0-4	-1063	2 0-2	0	0 0 0
ZN	CO3-	909	1 1 0	0	0 0 0	0	0 0 0	439	1 1 0	1135	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	SO4	0	0 0 0	0	0 0 0	0	0 0 0	149	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	CL	0	0 0 0	0	0 0 0	0	0 0 0	-5	1 1 0	102	1 2 0	-17	1 3 0	-750	1 1-1	-25	1 4 0	0	0 0 0
ZN	NH3	0	0 0 0	0	0 0 0	0	0 0 0	220	1 1 0	449	1 2 0	689	1 3 0	889	1 4 0	0	0 0 0	0	0 0 0
ZN	PO4	3191	3 2 0	0	0 0 0	0	0 0 0	1367	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	SIO3	1759	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	1719	1 1 0	2040	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
ZN	OH	-1283	1 0-2	0	0 0 0	0	0 0 0	-929	1 0-1	-2456	1 0-3	-4097	1 0-4	-1723	1 0-2	-883	2 0-1	0	0 0 0
CH	CO3-	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	SO4	0	0 0 0	0	0 0 0	0	0 0 0	134	1 1 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	CL	0	0 0 0	0	0 0 0	0	0 0 0	12	1 1 0	-112	1 2 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	NH3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	PO4	0	0 0 0	0	0 0 0	0	0 0 0	1952	1 1 1	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	SIO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	EDTA	0	0 0 0	0	0 0 0	0	0 0 0	2409	1 1 0	2432	1 1 1	1668	1 1-1	0	0 0 0	0	0 0 0	0	0 0 0
CH	NO3	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	CRO4	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0	0	0 0 0
CH	OH	-1244	1 0-3	0	0 0 0	0	0 0 0	-440	1 0-1	-958	1 0-2	-2447	1 0-4	0	0 0 0	0	0 0 0	0	0 0 0

Figure 2c. Thermodynamic data at 25°C shown for comparison

```
INPUT DATA

THESE COMPUTATIONS INVOLVE 10 METALS. 10 LIGANDS.  128 COMPLEXES AND   29 POSSIBLE SOLIDS.

IONIC STRENGTH = 0.9999996E-01
IONIC STRENGTH CORRECTIONS WILL BE PERFORMED.

 2 DIFFERENT CASES ARE TREATED.
THE CONDITIONS FOR THE DIFFERENT CASES ARE:

                METAL CONCENTRATIONS

NAME  REF. #      FREE   TOTAL 1   TOTAL 2
CONCENTRATIONS IN -LOG(MOLES/L)

CA        1      4.130     4.130     4.130

MG        2      4.340     4.340     4.340

K         4      4.640     4.640     4.640

NA        5      3.280     3.280     3.280

FE3       6     21.000     7.700     7.700

FE2       7      6.370     6.370     6.370

CU        9     28.000     6.930     6.930

ZN       12      6.610     6.610     6.610

CR       19     14.000     6.660     6.660

                LIGAND CONCENTRATIONS

NAME  REF. #      FREE   TOTAL 1   TOTAL 2
CONCENTRATIONS IN -LOG(MOLES/L)

CO3-      1      3.430     3.430     3.430

SO4       2      4.440     4.440     4.440

CL        3      3.400     3.400     3.400

NH3       7      4.010     4.010     4.010

PO4       9     12.000     6.490     6.490

SIO3     12     10.000     3.610     3.610

EDTA     28     20.000    20.000     6.570

NO3      57      4.600     4.600     4.600

CHO4     59      9.000     9.000     9.000

                          CASE  1   CASE  2


FIXED PH                  8.000     0.0
```

Figure 2d. Input data printout

```
CASE NUMBER  1


CASE PROGRESS
NUMBER OF ITERATIONS =   7
SOLID  FE3  OH    1 0-3  PRECIPITATES.
NUMBER OF ITERATIONS =   9
SOLID  ZN   SIO3  1 1 0  PRECIPITATES.
NUMBER OF ITERATIONS =  14
SOLID  CU   CO3-  2 1-2  PRECIPITATES.
NUMBER OF ITERATIONS =  16
NUMBER OF ITERATIONS =  25
NUMBER OF ITERATIONS =  27


CHARGE ON SOLUTION (MOLES/L)
    POSITIVE 0.174E-02
    NEGATIVE-0.173E-02
    TOTAL    0.123E-04

LIGAND TOTAL CONCENTRATIONS ADJUSTED BY A FACTOR OF 1.007
NUMBER OF ITERATIONS =  24


CHARGE ON SOLUTION (MOLES/L)
    POSITIVE 0.175E-02
    NEGATIVE-0.174E-02
    TOTAL    0.681E-05


IONIC STRENGTH =  1.0340665E-03

FIXED PH = 8.000          COMPUTED TOTH = 0.9603139E-03          SOLUBLE H =  0.9603936E-03

                FREE CONC        -LOG FREE CONC      TOT CONC        -LOG TOT CONC      REMAINDER

                MOLES/L                              MOLES/L                            MOLES/L
CA          7.3592309E-05          4.13317       7.4131327E-05          4.13000      3.6237680E-13
MG          4.5426932E-05          4.34269       4.5709006E-05          4.34000     -5.4010574E-12
K           2.2903099E-05          4.64011       2.2908745E-05          4.64000     -4.6433968E-12
NA          5.2472367E-04          3.28007       5.2480842E-04          3.28000     -7.7307050E-12
FE3         2.0774336E-21         20.68248       1.9952950E-08          7.69999      0.0
FE2         4.1151907E-07          6.38561       4.2658104E-07          6.37000      3.9425846E-14
CU          1.4915169E-08          7.85452       1.1749034E-07          6.93000      0.0
ZN          1.4454943E-08          7.83998       2.3332711E-07          6.63204     -1.1766645E-08
OH          1.5630841E-15         14.80602       2.1877867E-07          6.66000      0.0
CO3-        7.6807873E-07          6.11459       3.7418446E-04          3.42691      8.6338048E-11
SO4         3.5916426E-05          4.44471       3.6566722E-05          4.43691     -4.3827858E-12
CL          4.0093879E-04          3.39692       4.0094578E-04          3.39691     -3.6979489E-11
NH3         4.0794930E-06          5.38939       9.8420729E-05          4.00691      4.3655746E-11
PO4         9.5839257E-12         11.01845       3.2590378E-07          6.48691      1.7709220E-12
SIO3        2.9197811E-11         10.53466       2.4722144E-04          3.60691      0.0
EDTA        7.3853665E-34         33.13162       1.0071444E-20         19.99690      1.2129605E-27
NO3         2.5298024E-05          4.59691       2.5298024E-05          4.59691      0.0
CRO4        9.7983421E-10          9.00885       1.0071430E-09          8.99691     -3.1896190E-16

SOLID                    MOLES PER LITER OF SOLUTION

FE3  OH    1 0-3              1.9878716E-08



CU   CO3-  2 1-2              9.9416226E-09
ZN   SIO3  1 1 0              2.1395681E-07
```

Figure 2e. Case progress for first case

SPECIATION OF METALS AND LIGANDS

SUM OF CONCENTRATIONS OF ALL SPECIES REPORTED AS -LOG(M)

	FREE MET	CO3-	SO4	CL	NH3	PO4	SIO3	EDTA	NO3	CRO4	OH
FREE LIG		6.11	4.44	3.40	5.39	11.02	10.53	33.13	4.60	9.01	6.14
H	8.00	3.43	10.57	*****	4.03	6.50	3.61	29.90	*****	10.56	*****
CA	4.13	6.81	6.42	*****	9.62	8.16	*****	24.92	*****	*****	8.87
MG	4.34	7.13	6.73	*****	9.62	8.27	*****	28.62	*****	*****	7.78
K	4.64	*****	8.25	*****	*****	*****	*****	*****	*****	*****	*****
NA	3.28	8.26	7.10	*****	*****	*****	*****	33.74	*****	*****	*****
FE3	20.68	*****	21.31	22.74	*****	19.28	15.87	24.94	*****	*****	10.13
FE2	6.39	*****	8.76	8.95	10.47	9.61	*****	23.07	*****	*****	7.92
CU	7.86	7.24	10.05	8.22	9.24	11.09	*****	20.04	*****	*****	7.58
ZN	7.84	8.75	10.03	10.21	11.03	11.87	*****	22.22	*****	*****	8.53
CR	14.81	*****	16.74	17.50	*****	12.60	*****	21.07	*****	*****	6.66

Figure 2f. Speciation of metals for first case

CONCENTRATIONS OF COMPLEXES

METAL	LIGAND	CONC. -LOG(M)	M L H	CONC. -LOG(M)	M L H	CONC. -LOG(M)	M L H	CONC. -LOG(M)	M L H	CONC. -LOG(M)	M L H	CONC. -LOG(M)	M L H
H	CO3-	3.43	0 1 1	5.49	0 1 2								
H	SO4	10.57	0 1 1										
H	NH3	4.03	0 1 1										
H	PO4	6.66	0 1 1	7.02	0 1 2	13.18	0 1 3						
H	SIO3	5.49	0 1 1	3.61	0 1 2								
H	EDTA	29.95	0 1 1	30.84	0 1 2	35.79	0 1 3	41.61	0 1 4				
H	CRO4	10.56	0 1 1	18.79	0 1 2	19.50	0 2 2	27.55	0 2 3				
CA	CO3-	7.17	1 1 0	7.07	1 1 1								
CA	SO4	6.42	1 1 0										
CA	NH3	9.62	1 1 0	15.61	1 2 0	21.80	1 3 0	28.29	1 4 0				
CA	PO4	8.26	1 1 1	8.84	1 1 0								
CA	EDTA	24.92	1 1 0	29.67	1 1 1								
CA	OH	8.87	1 0-1										
MG	CO3-	7.68	1 1 0	7.27	1 1 1								
MG	SO4	6.73	1 1 0										
MG	NH3	9.62	1 1 0	14.92	1 2 0	20.81	1 3 0	26.90	1 4 0				
MG	PO4	8.27	1 1 1										
MG	EDTA	28.63	1 1 0	32.18	1 1 1								
MG	OH	7.78	1 0-1	25.34	4 0-4								
K	SO4	8.25	1 1 0										
NA	CO3-	8.26	1 1 0										
NA	SO4	7.10	1 1 0										
NA	EDTA	33.74	1 1 0										
FE3	SO4	21.32	1 1 0	24.42	1 2 0								
FE3	CL	22.74	1 1 0	25.53	1 2 0	29.76	1 3 0						
FE3	PO4	19.28	1 1 1										
FE3	SIO3	15.87	1 1 1										
FE3	EDTA	25.39	1 1 0	31.71	1 1 1	25.14	1 1-1	27.15	1 1-2				
FE3	OH	14.95	1 0-1	10.49	1 0-2	10.38	1 0-4	28.28	2 0-2				
FE2	SO4	8.76	1 1 0										
FE2	CL	8.95	1 1 0										
FE2	NH3	10.48	1 1 0	15.06	1 2 0	24.34	1 4 0						
FE2	PO4	9.62	1 1 1	11.31	1 1 2								
FE2	EDTA	23.07	1 1 0	27.72	1 1 1								
FE2	OH	7.92	1 0-1	14.41	1 0-3	20.75	1 0-4						
CU	CO3-	7.30	1 1 0	10.31	1 2 0	9.59	1 1 1	11.02	1 1-2				
CU	SO4	10.05	1 1 0										
CU	CL	10.92	1 1 0	12.54	1 2 0	16.24	1 3 0	20.11	1 4 0	8.22	1 1-1		
CU	NH3	9.25	1 1 0	11.14	1 2 0	13.72	1 3 0	17.61	1 4 0				
CU	PO4	11.09	1 1 1	13.78	1 1 2								
CU	EDTA	20.04	1 1 0	24.49	1 1 1	24.05	1 1-1						
CU	OH	7.60	1 0-1	9.20	1 0-2	10.68	1 0-3	15.43	1 0-4	10.06	2 0-2		
ZN	CO3-	8.78	1 1 0	9.87	1 1 1								
ZN	SO4	10.03	1 1 0										
ZN	CL	10.90	1 1 0	13.03	1 2 0	17.62	1 3 0	10.31	1 1-1	21.29	1 4 0		
ZN	NH3	11.03	1 1 0	14.12	1 2 0	17.11	1 3 0	20.50	1 4 0				
ZN	PO4	11.87	1 1 1										
ZN	EDTA	22.22	1 1 0	26.68	1 1 1								
ZN	OH	8.88	1 0-1	12.26	1 0-3	17.01	1 0-4	8.79	1 0-2	16.66	2 0-1		
CR	SO4	10.74	1 1 0										
CR	CL	17.50	1 1 0	21.76	1 2 0								
CR	PO4	12.60	1 1 1										
CR	EDTA	21.51	1 1 0	27.14	1 1 1	21.26	1 1-1						
CR	OH	10.93	1 0-1	7.72	1 0-2	6.70	1 0-4						

Figure 2g. Concentration of complexes for first case

PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.5 % SHOWN

CA		
	99.3 %	AS A FREE METAL
	0.5 %	COMPLEXED WITH SO4
MG		
	96.4 %	AS A FREE METAL
K		
	100.0 %	AS A FREE METAL
NA		
	100.0 %	AS A FREE METAL
FE3		
	99.6 %	IN SOLID FORM WITH OH
FE2		
	96.5 %	AS A FREE METAL
	2.8 %	COMPLEXED WITH OH
CU		
	11.8 %	AS A FREE METAL
	43.3 %	COMPLEXED WITH CO3-
	15.9 %	IN SOLID FORM WITH CO3-
	5.1 %	COMPLEXED WITH CL
	22.3 %	COMPLEXED WITH OH
ZN		
	6.2 %	AS A FREE METAL
	0.8 %	COMPLEXED WITH CO3-
	91.7 %	IN SOLID FORM WITH SIO3
	1.3 %	COMPLEXED WITH OH
CH		
	100.0 %	COMPLEXED WITH OH
CO3-		
	99.7 %	COMPLEXED WITH H
SO4		
	94.2 %	AS A FREE LIGAND
	1.0 %	COMPLEXED WITH CA
	0.5 %	COMPLEXED WITH MG
CL		
	100.0 %	AS A FREE LIGAND
NH3		
	4.1 %	AS A FREE LIGAND
	95.9 %	COMPLEXED WITH H
PO4		
	96.2 %	COMPLEXED WITH H
	2.1 %	COMPLEXED WITH CA
	1.6 %	COMPLEXED WITH MG
SIO3		
	95.9 %	COMPLEXED WITH H
EDTA		
	90.8 %	COMPLEXED WITH CU
	0.6 %	COMPLEXED WITH ZN
	8.5 %	COMPLEXED WITH CH
NO3		
	100.0 %	AS A FREE LIGAND
CRO4		
	97.1 %	AS A FREE LIGAND
	2.9 %	COMPLEXED WITH H

Figure 2h. Distribution of metals and ligands for first case

SATURATION OF SOLIDS

SOLID				DEGREE OF SATURATION (LOG)
CA	CO3-	1	1 0	-1.973
MG	CO3-	1	1 0	-3.083

Figure 2i Saturation of selected solids as log (ion product/ solubility product)

```
CASE NUMBER  2


CASE PROGRESS
NUMBER OF ITERATIONS =   3
SOLID  CU   CO3-  2 1-2  DISSOLVES.
NUMBER OF ITERATIONS =   9


CHARGE ON SOLUTION (MOLES/L)
    POSITIVE 0.174E-02
    NEGATIVE-0.173E-02
    TOTAL    0.118E-04

LIGAND TOTAL CONCENTRATIONS ADJUSTED BY A FACTOR OF 1.007
NUMBER OF ITERATIONS =  12


CHARGE ON SOLUTION (MOLES/L)
    POSITIVE 0.175E-02
    NEGATIVE-0.174E-02
    TOTAL    0.653E-05


IONIC STRENGTH =  1.0343057E-03

FIXED PH = 8.000          COMPUTED TOTH = 0.9605822E-03          SOLUBLE H =  0.9606418E-03

                FREE CONC          -LOG FREE CONC      TOT CONC          -LOG TOT CONC      REMAINDER

                MOLES/L                                MOLES/L                              MOLES/L
CA          7.3592382E-05          4.13317          7.4131312E-05          4.13000      -1.4025892E-11
MG          4.5426990E-05          4.34269          4.5709006E-05          4.34000      -1.2825296E-11
K           2.2903099E-05          4.64011          2.2908745E-05          4.64000      -6.2811978E-12
NA          5.2472367E-04          3.28007          5.2480819E-04          3.28000      -3.1377567E-11
FE3         2.0774336E-21         20.68248          1.9952950E-08          7.69999       0.0
FE2         4.0841911E-07          6.38889          4.2658093E-07          6.37000      -1.2402828E-13
CU          4.5911541E-10          9.33807          1.1748978E-07          6.93000      -3.3852877E-12
ZN          1.4458692E-08          7.83987          2.4392943E-07          6.61274      -1.4815100E-09
CH          6.2921292E-16         15.20120          2.1877588E-07          6.66000      -6.0822458E-12
CO3-        7.6797397E-07          6.11465          3.7407409E-04          3.42704       1.8371793E-10
SO4         3.5905920E-05          4.44483          3.6555924E-05          4.43704      -1.7271323E-12
CL          4.0082610E-04          3.39704          4.0082750E-04          3.39704      -1.1921420E-11
NH3         4.0783234E-06          5.38952          9.8391843E-05          4.00704      -5.8207661E-11
PO4         9.5813713E-12         11.01857          3.2580425E-07          6.48704      -1.4691703E-12
SIO3        2.9190678E-11         10.53476          2.4714856E-04          3.60704       0.0
EDTA        2.7970497E-19         18.55330          2.7099162E-07          6.56704      -8.7534051E-12
NO3         2.5290545E-05          4.59704          2.5290545E-05          4.59704       0.0
CHO4        9.7954467E-10          9.00897          1.0048457E-09          8.99703      -1.3650815E-17

SOLID                    MOLES PER LITER OF SOLUTION

FE3  OH    1 0-3              1.9835291E-08
ZN   SIO3  1 1 0              2.0184962E-07
```

Figure 2j. Case progress for second case

```
PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.5 % SHOWN

CA
      99.3 %  AS A FREE METAL
       0.5 %  COMPLEXED WITH SO4

MG
      99.4 %  AS A FREE METAL

K
     100.0 %  AS A FREE METAL

NA
     100.0 %  AS A FREE METAL

FE3
      94.4 %  IN SOLID FORM WITH OH

FE2
      95.7 %  AS A FREE METAL
       0.8 %  COMPLEXED WITH EDTA
       2.8 %  COMPLEXED WITH OH

CU
       1.4 %  COMPLEXED WITH CO3-
      97.3 %  COMPLEXED WITH EDTA
       0.7 %  COMPLEXED WITH OH

ZN
       5.9 %  AS A FREE METAL
       0.7 %  COMPLEXED WITH CO3-
      82.7 %  IN SOLID FORM WITH SIO3
       9.3 %  COMPLEXED WITH EDTA
       1.2 %  COMPLEXED WITH OH

CH
      59.7 %  COMPLEXED WITH EDTA
      40.3 %  COMPLEXED WITH OH

CO3-
      99.7 %  COMPLEXED WITH H

SO4
      98.2 %  AS A FREE LIGAND
       1.0 %  COMPLEXED WITH CA
       0.5 %  COMPLEXED WITH MG

CL
     100.0 %  AS A FREE LIGAND

NH3
       4.1 %  AS A FREE LIGAND
      95.9 %  COMPLEXED WITH H

PO4
      98.2 %  COMPLEXED WITH H
       0.1 %  COMPLEXED WITH CA
       1.6 %  COMPLEXED WITH MG

SIO3
      99.9 %  COMPLEXED WITH H

EDTA
       1.2 %  COMPLEXED WITH FE2
      96.2 %  COMPLEXED WITH CU
       0.4 %  COMPLEXED WITH ZN
      98.2 %  COMPLEXED WITH CH

NO3
     100.0 %  AS A FREE LIGAND

CHO4
      97.3 %  AS A FREE LIGAND
       2.7 %  COMPLEXED WITH H
```

Figure 2k. Distribution of metals and ligands for second case

```
PRIMARY DISTRIBUTION OF METALS AND LIGANDS

SPECIES OVER 0.5 % SHOWN

CA
      98.9 %  AS A FREE METAL
       0.6 %  COMPLEXED WITH CO3-
       0.5 %  COMPLEXED WITH SO4

MG
      99.1 %  AS A FREE METAL

K
     100.0 %  AS A FREE METAL

NA
     100.0 %  AS A FREE METAL

FE3
      94.9 %  IN SOLID FORM WITH OH

FE2
      95.7 %  AS A FREE METAL
       0.8 %  COMPLEXED WITH EDTA
       2.8 %  COMPLEXED WITH OH

CU
       3.6 %  COMPLEXED WITH CO3-
      95.1 %  COMPLEXED WITH EDTA
       0.7 %  COMPLEXED WITH OH

ZN
       5.9 %  AS A FREE METAL
       2.0 %  COMPLEXED WITH CO3-
      81.2 %  IN SOLID FORM WITH SIO3
       9.6 %  COMPLEXED WITH EDTA
       1.2 %  COMPLEXED WITH OH

CH
      60.6 %  COMPLEXED WITH EDTA
      39.4 %  COMPLEXED WITH OH

CO3-
       0.6 %  AS A FREE LIGAND
      99.3 %  COMPLEXED WITH H

SO4
      98.2 %  AS A FREE LIGAND
       1.1 %  COMPLEXED WITH CA
       0.5 %  COMPLEXED WITH MG

CL
     100.0 %  AS A FREE LIGAND

NH3
       5.8 %  AS A FREE LIGAND
      94.2 %  COMPLEXED WITH H

PO4
      96.8 %  COMPLEXED WITH H
       2.9 %  COMPLEXED WITH CA
       0.2 %  COMPLEXED WITH MG

SIO3
      99.9 %  COMPLEXED WITH H

EDTA
       1.2 %  COMPLEXED WITH FE2
      41.2 %  COMPLEXED WITH CU
       8.7 %  COMPLEXED WITH ZN
      48.9 %  COMPLEXED WITH CH

NO3
     100.0 %  AS A FREE LIGAND

CHO4
      97.3 %  AS A FREE LIGAND
       2.7 %  COMPLEXED WITH H
```

Figure 2l. Distribution of metals and ligands for second case at 25°C, for comparison

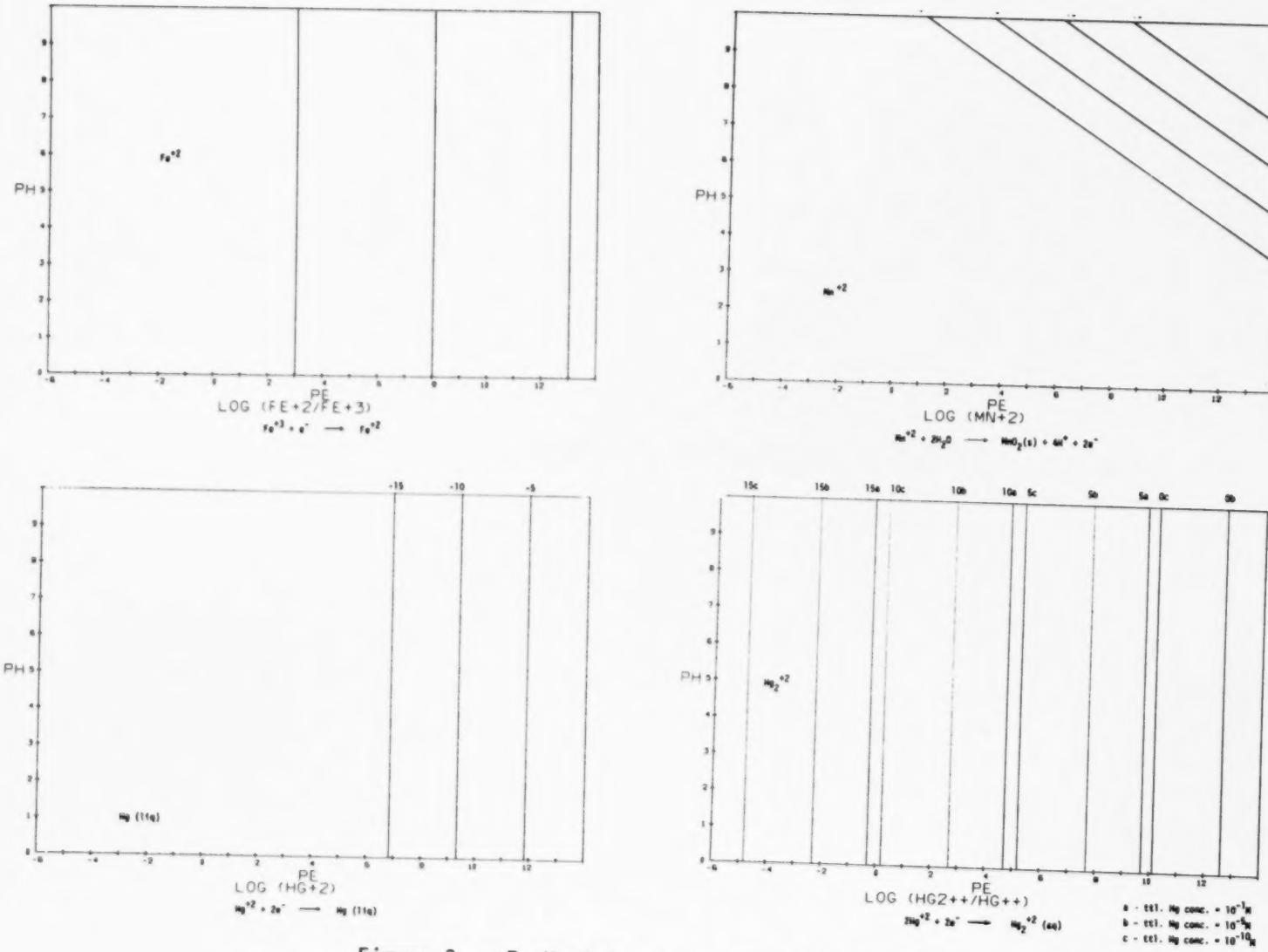


Figure 3. pE-pH plots of Fe, Mn and Hg species

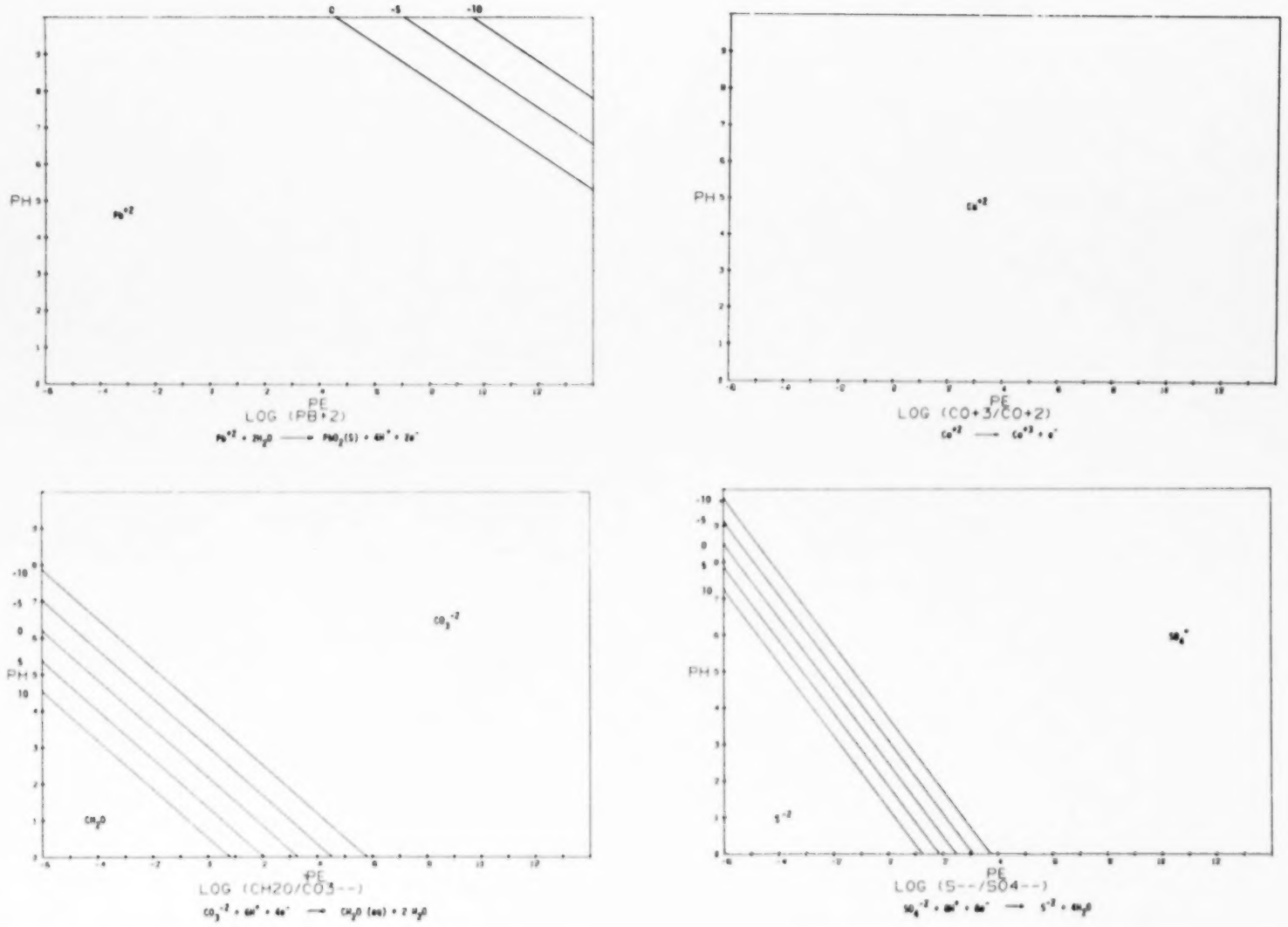


Figure 4. pE-pH plots of Pb, Co, $CO_3^{=}$ and S species

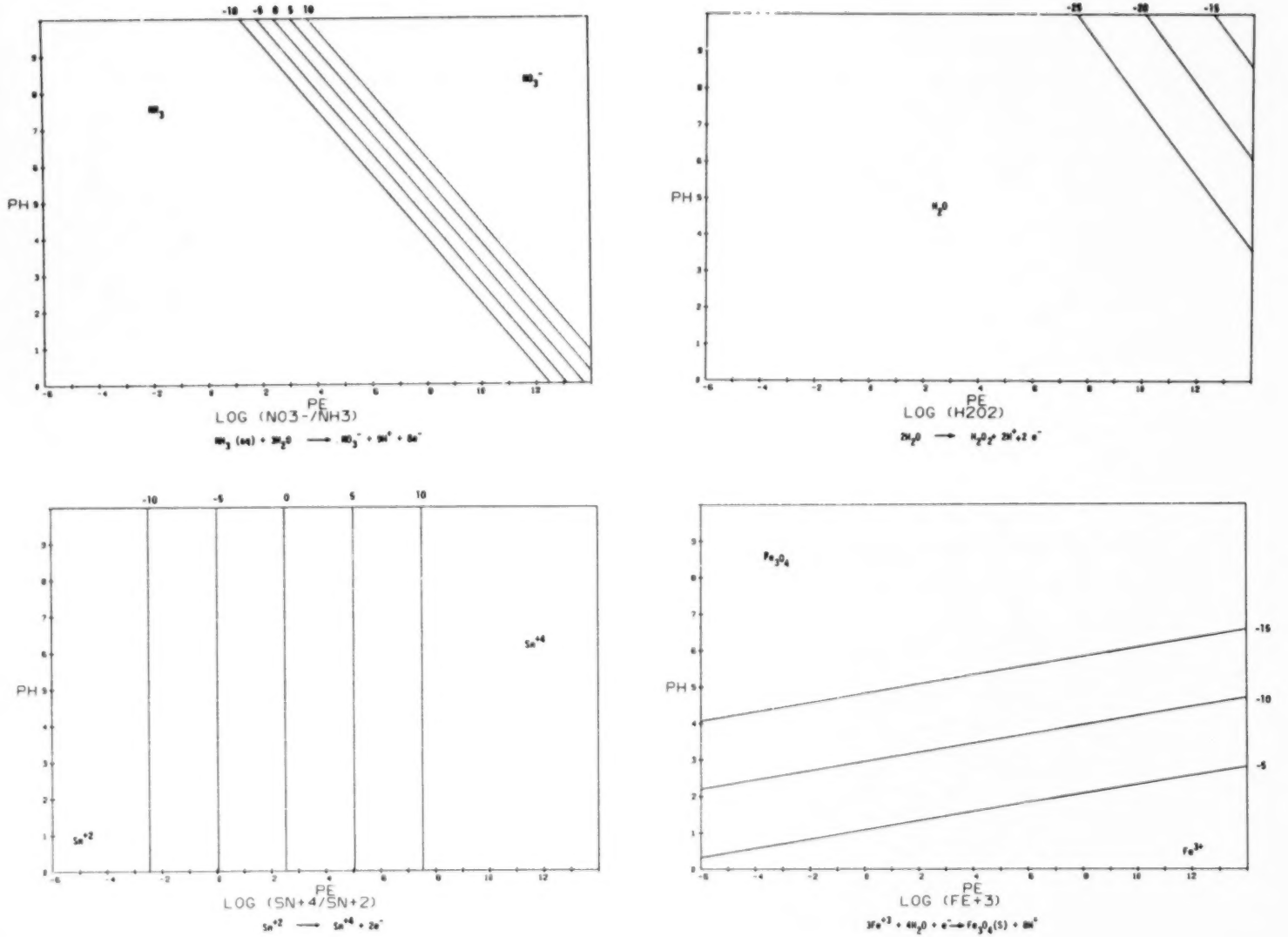


Figure 5. pE-pH plots of NH_3, H_2O_2, Sn and Fe species

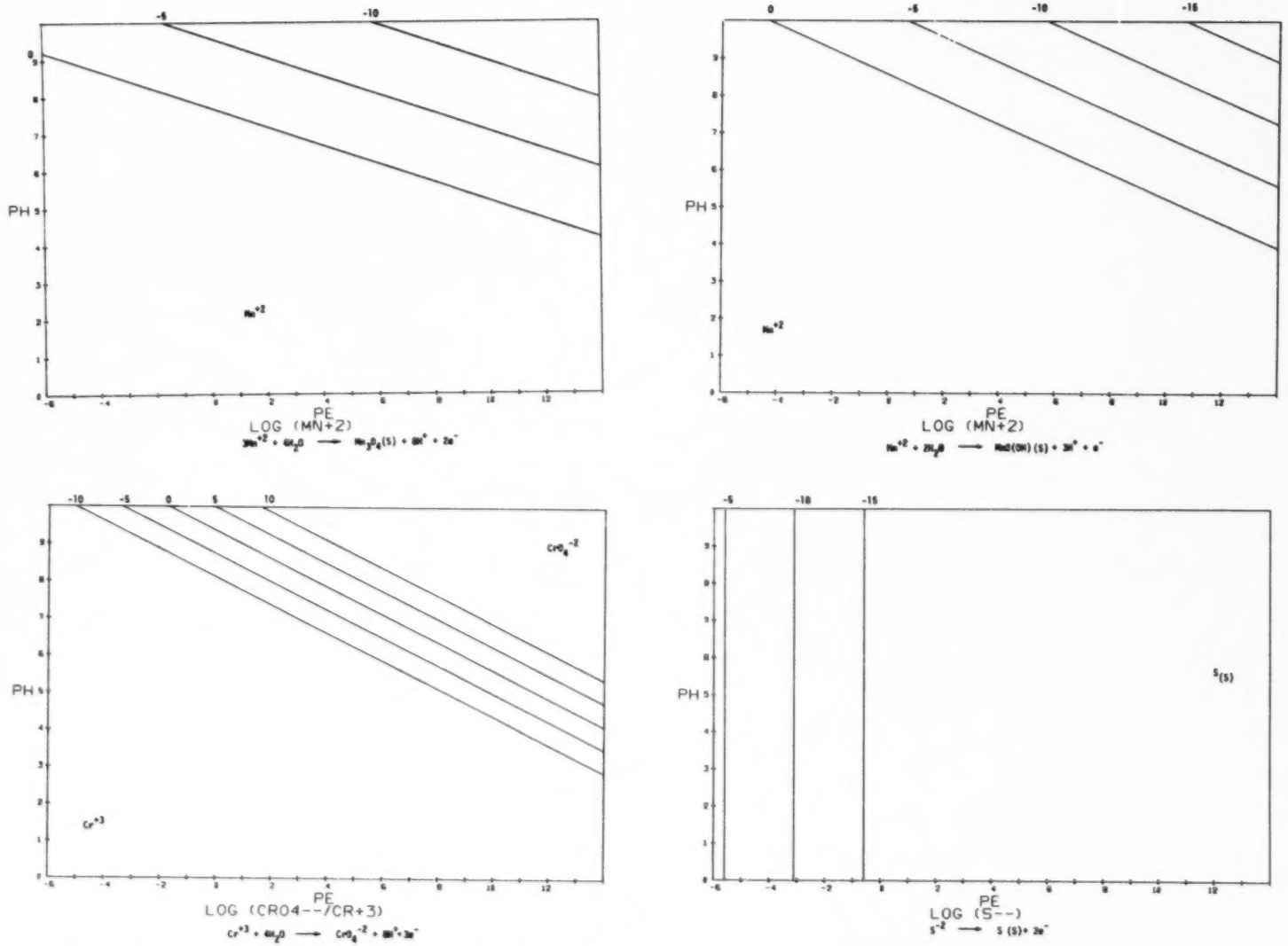


Figure 6. pE-pH plots of Mn, Cr and S species

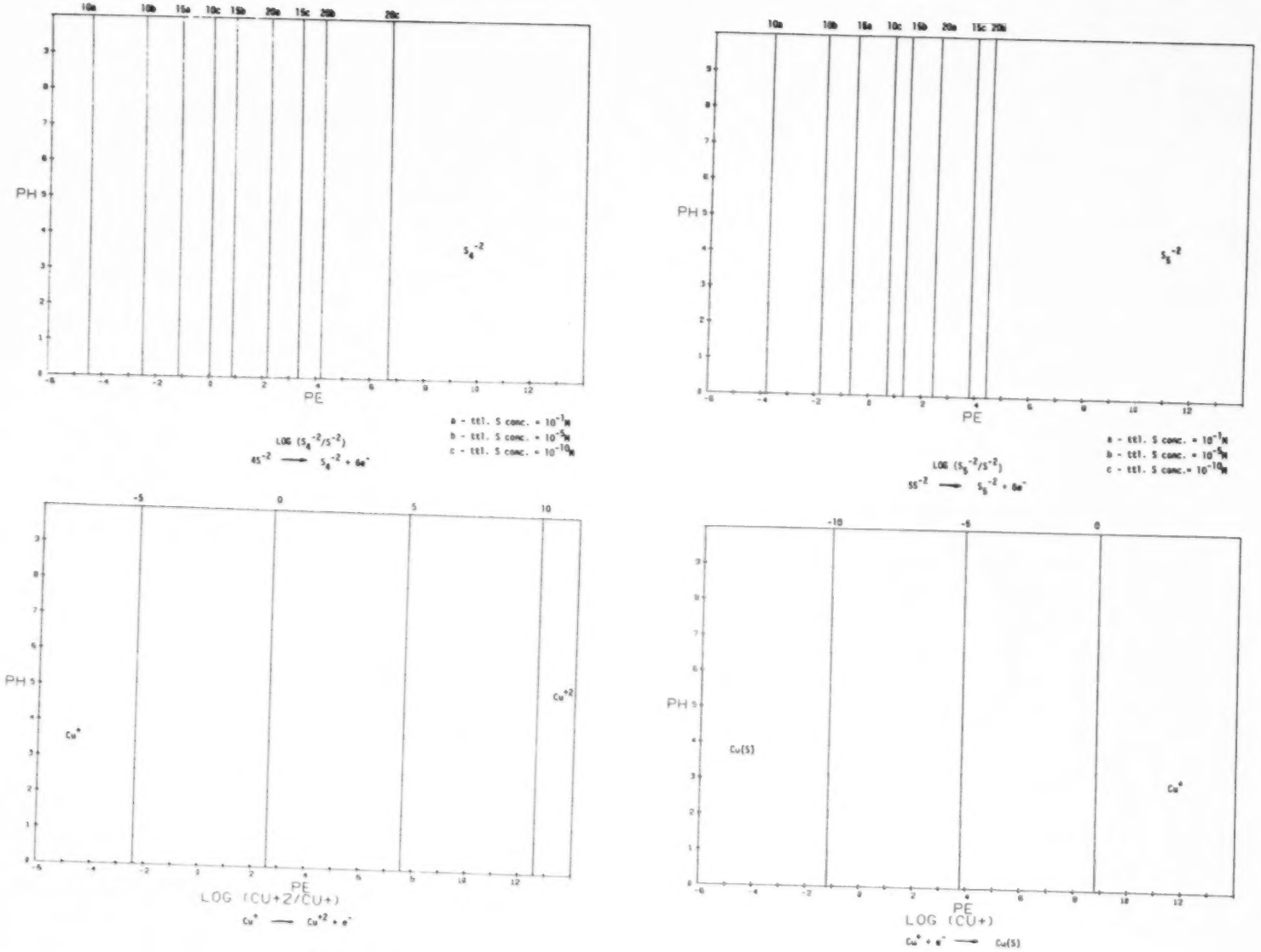
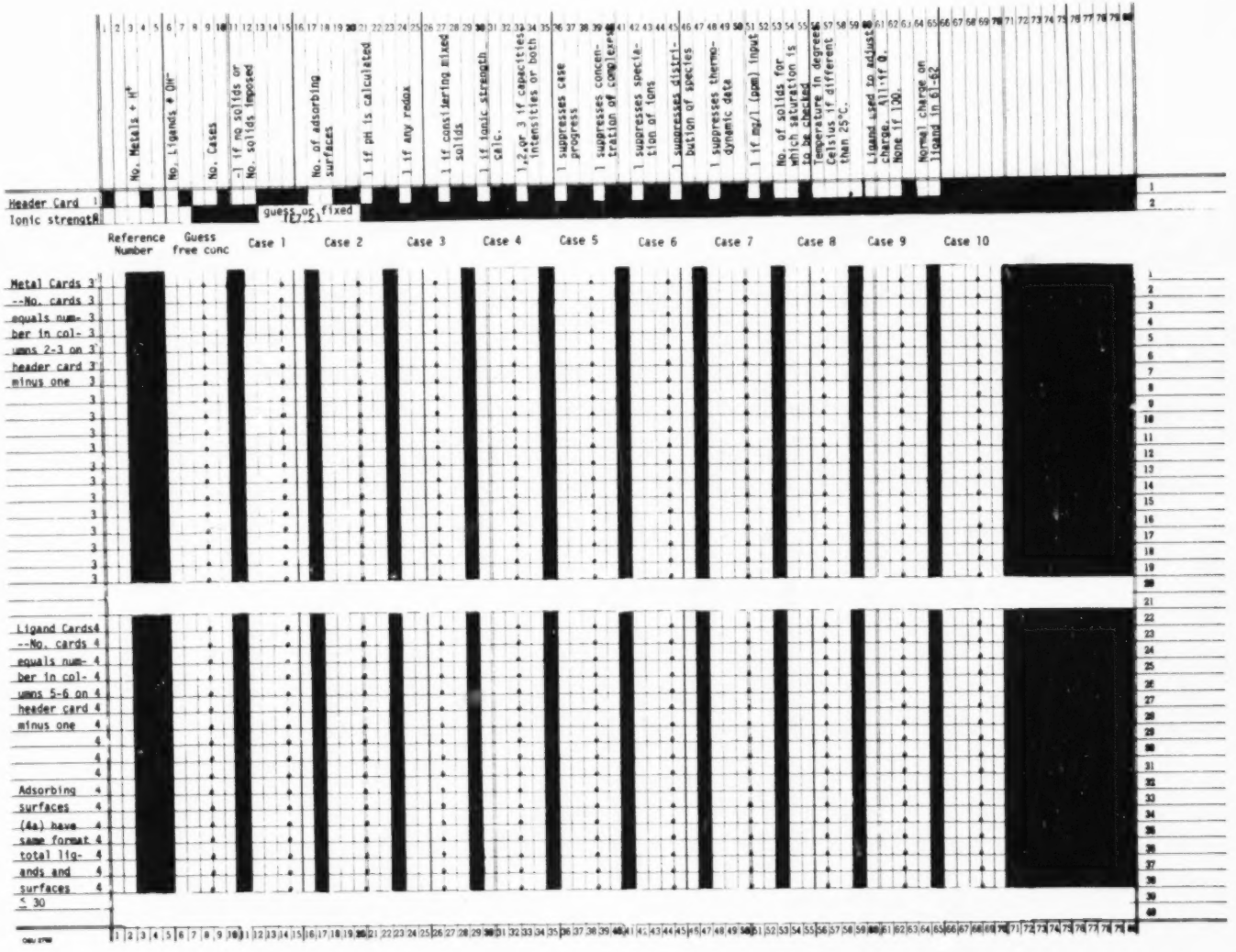
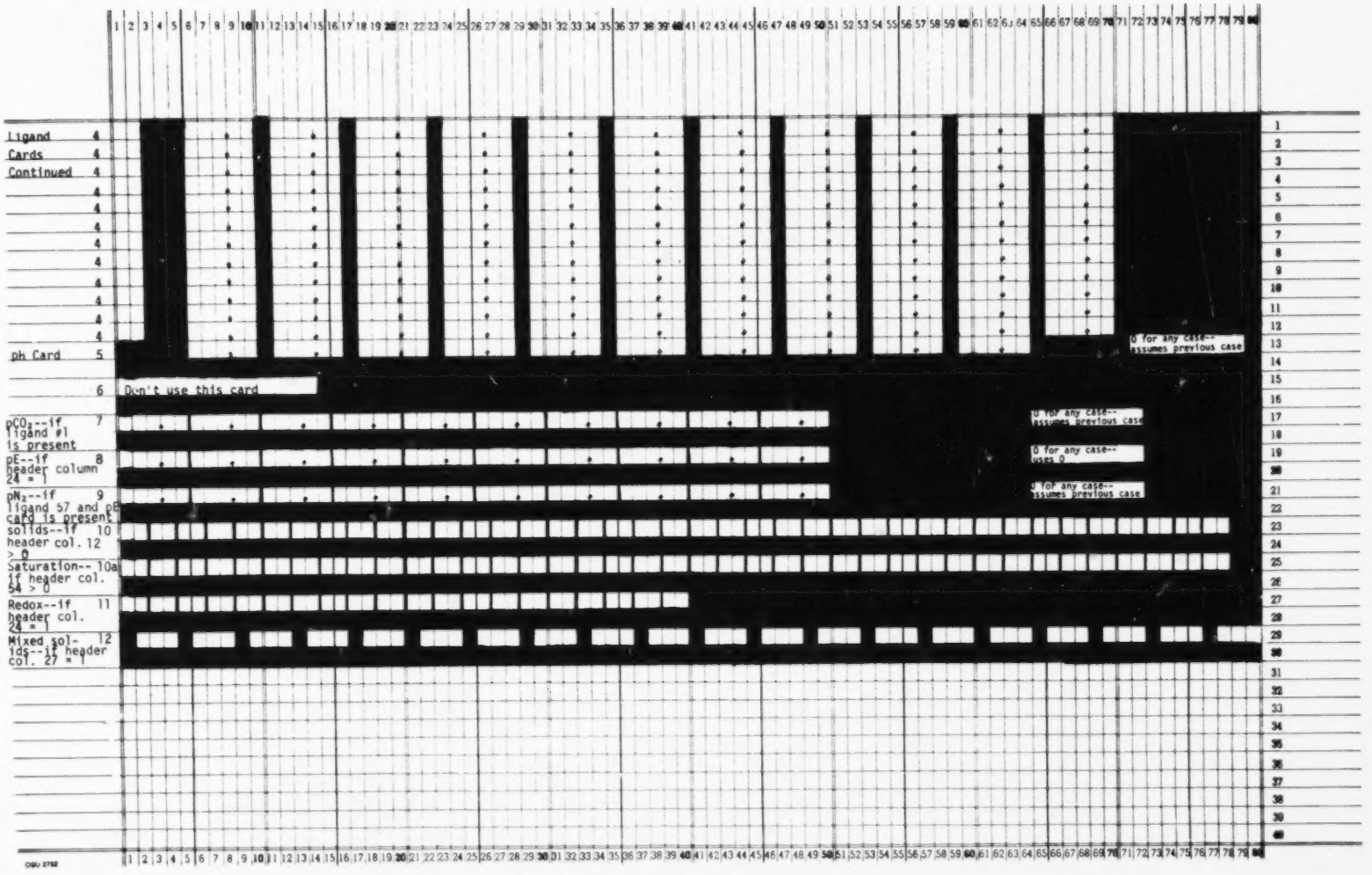
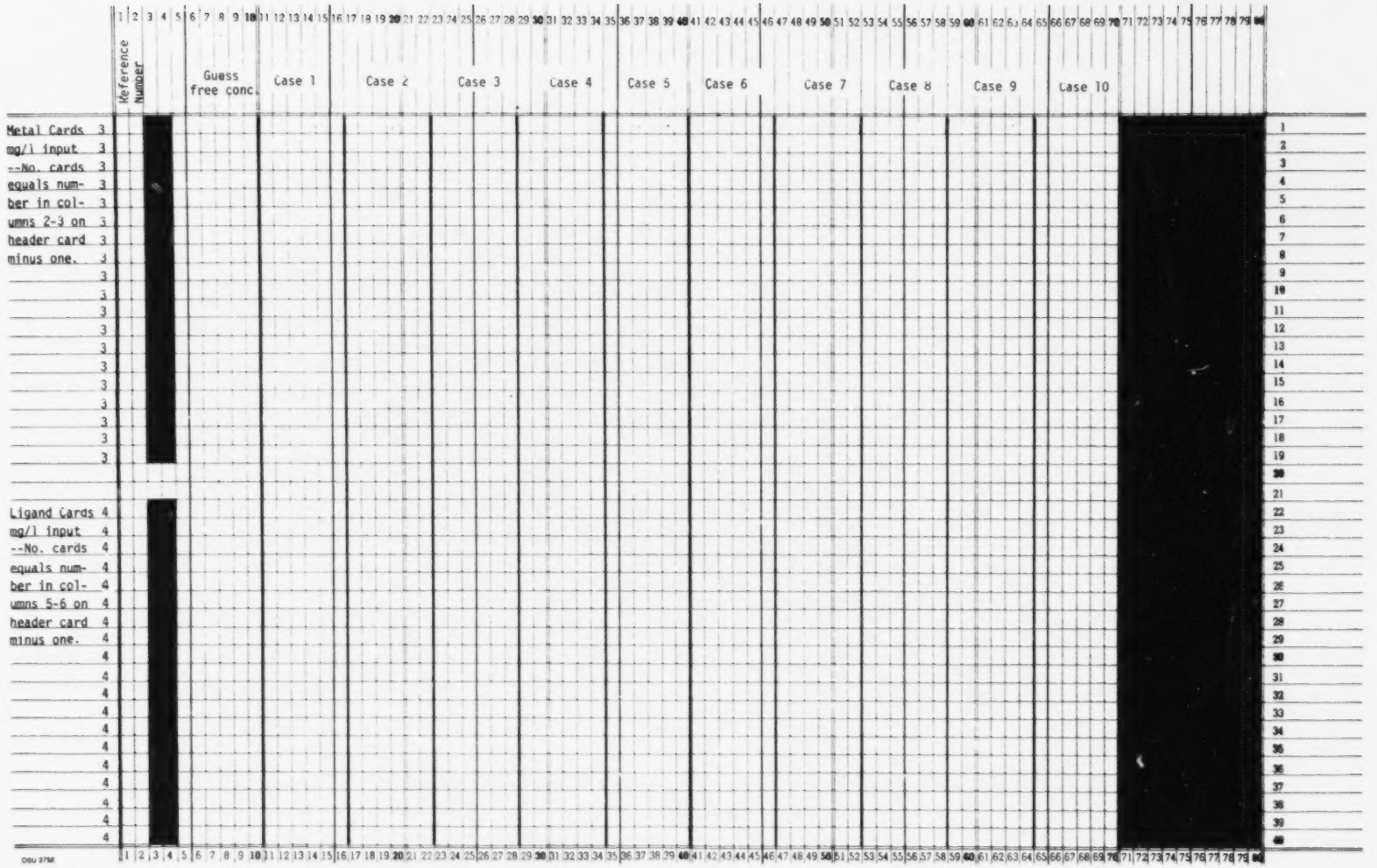


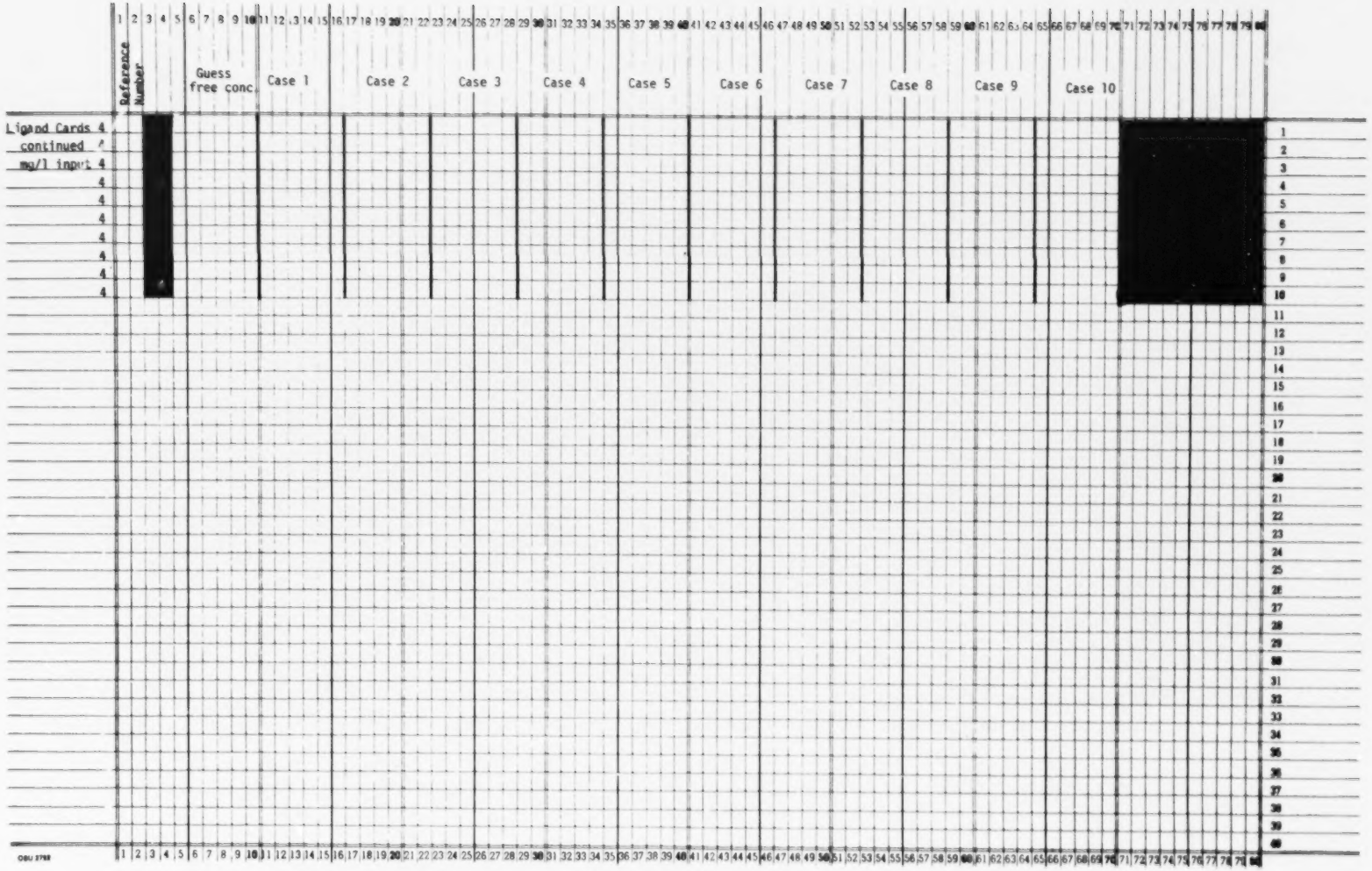
Figure 7. pE-pH plots of S and Cu species

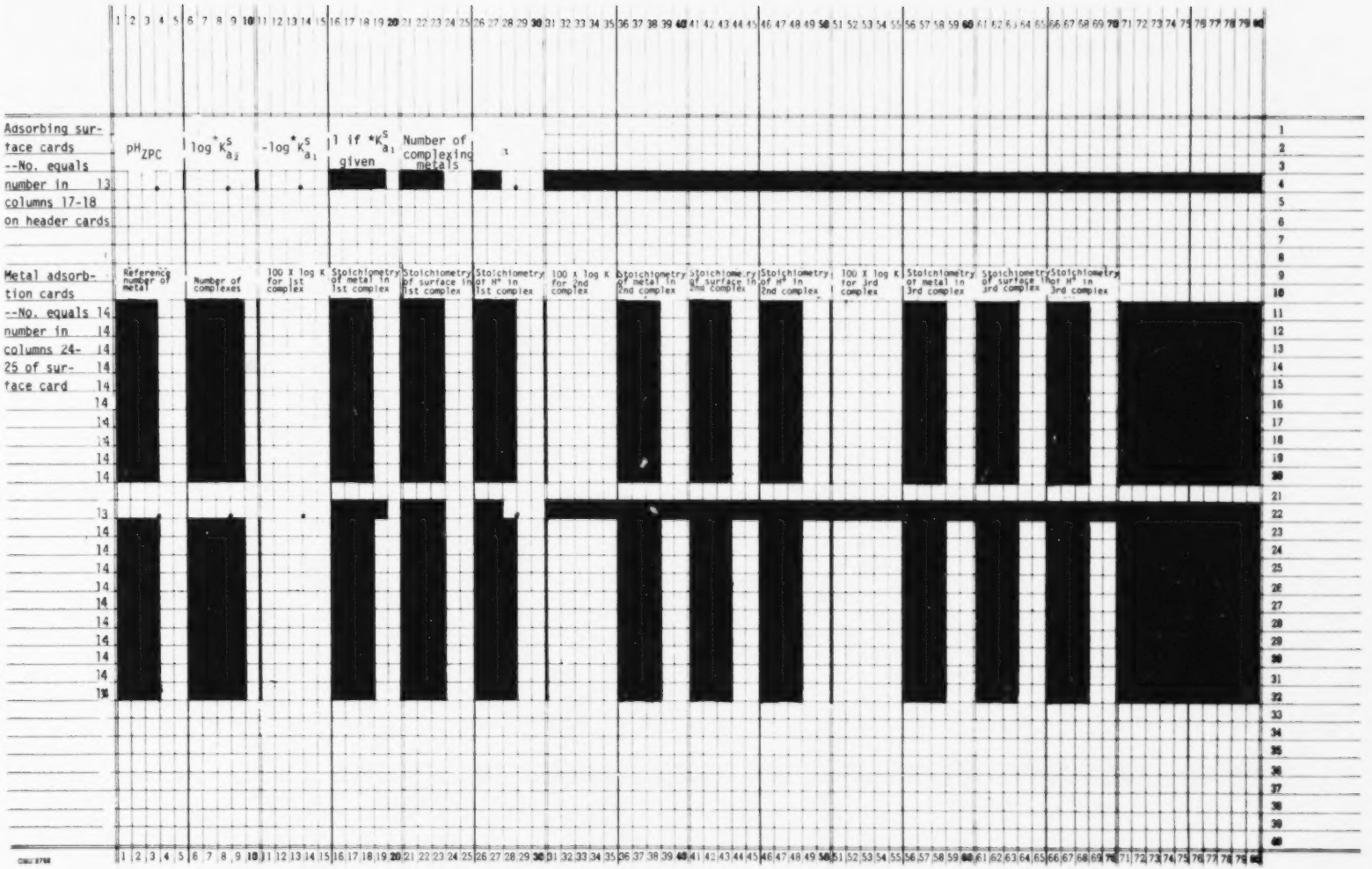
Appendix A. Input data sheets.

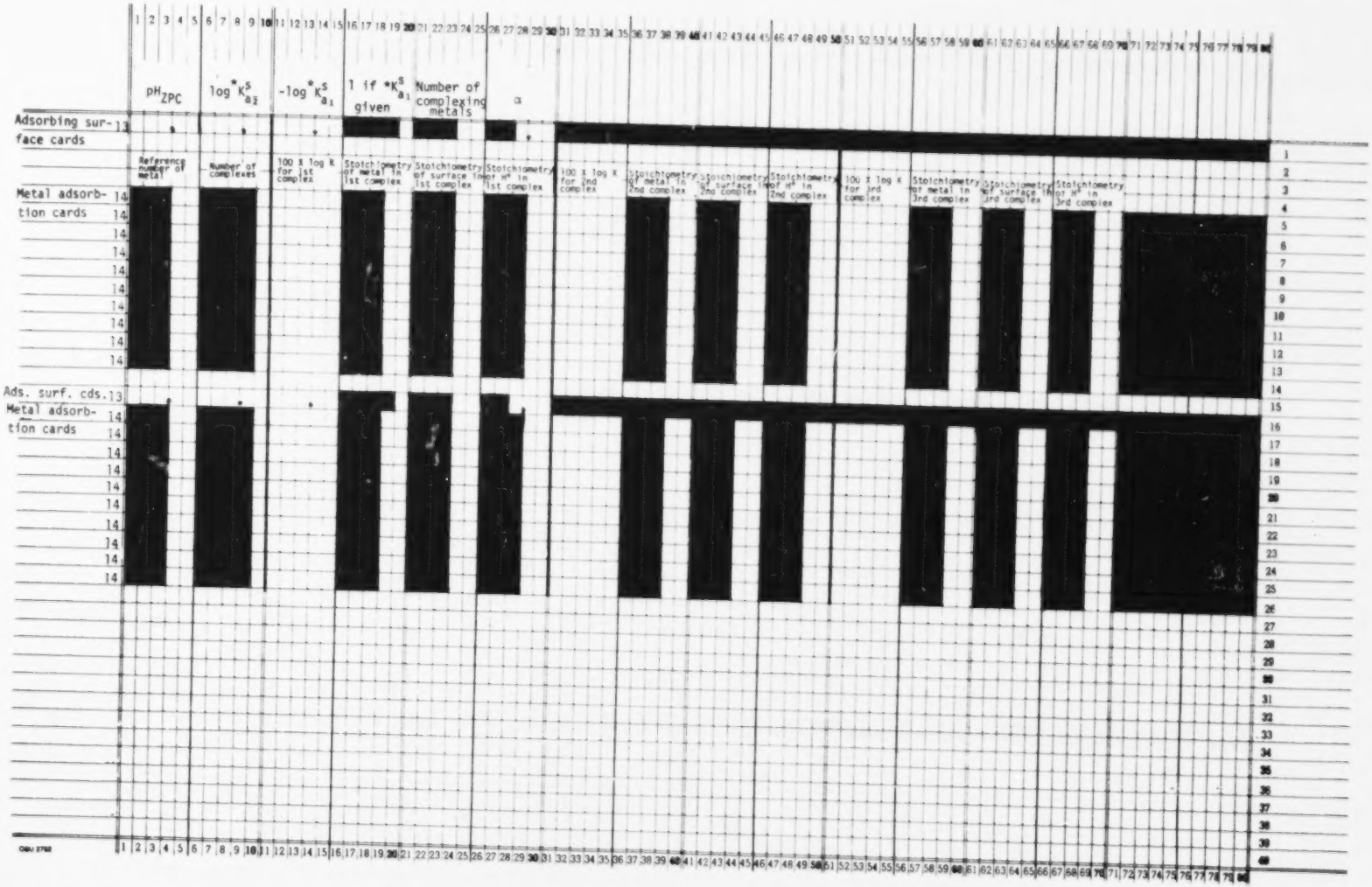


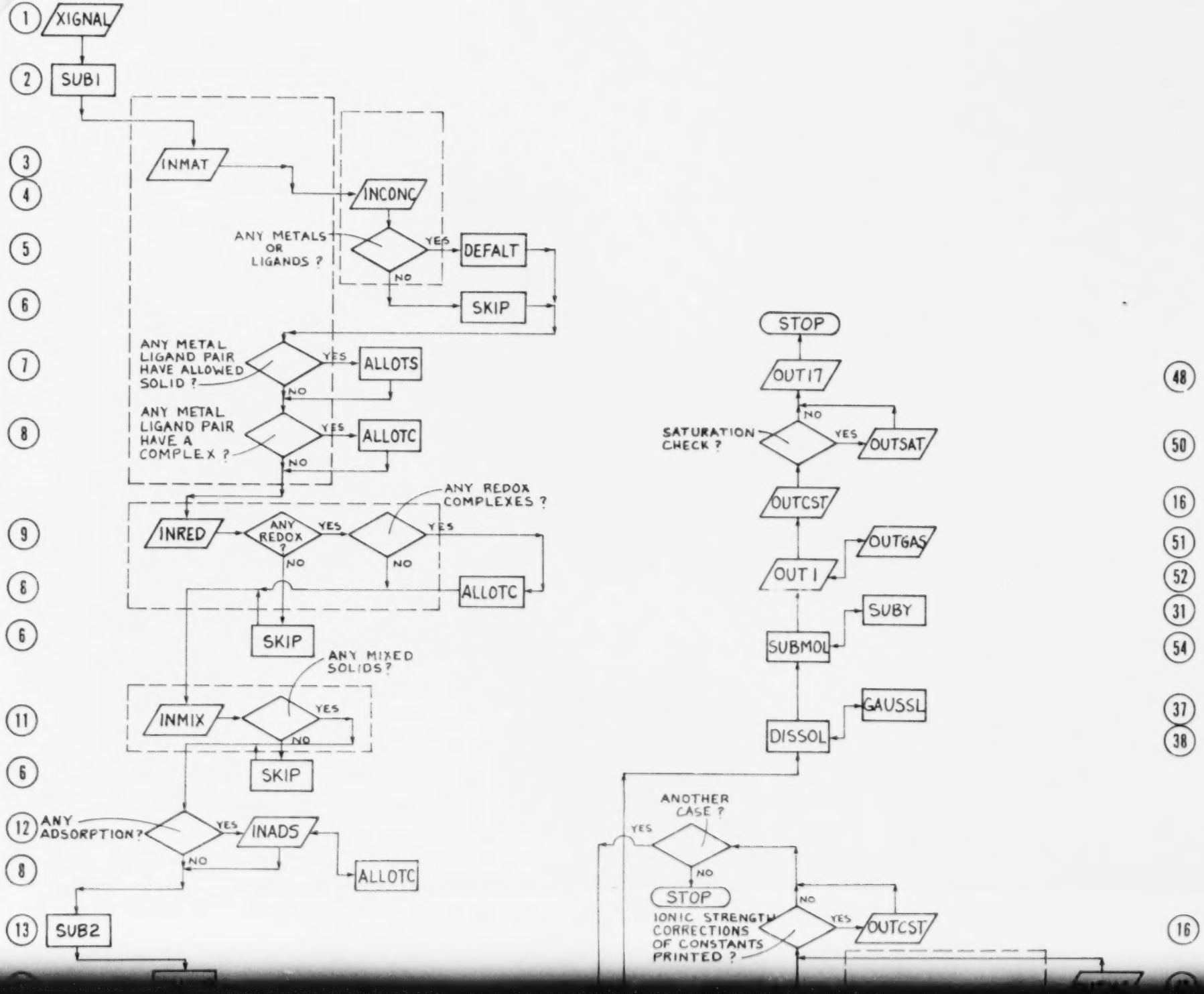

Ligand Cards Continued 4
pH Card 5
6
Don't use this card
pCO2--if ligand #1 is present 7
pE--if header column 24 = 1 8
pN2--if ligand 57 and pE card is present 9
solids--if header col. 12 > 0 10
Saturation--if header col. 54 > 0 10a
Redox--if header col. 24 = 1 11
Mixed solids--if header col. 27 = 1 12
0 for any case--assumes previous case
0 for any case--assumes previous case
0 for any case--uses 0
0 for any case--assumes previous case
OSU 2782

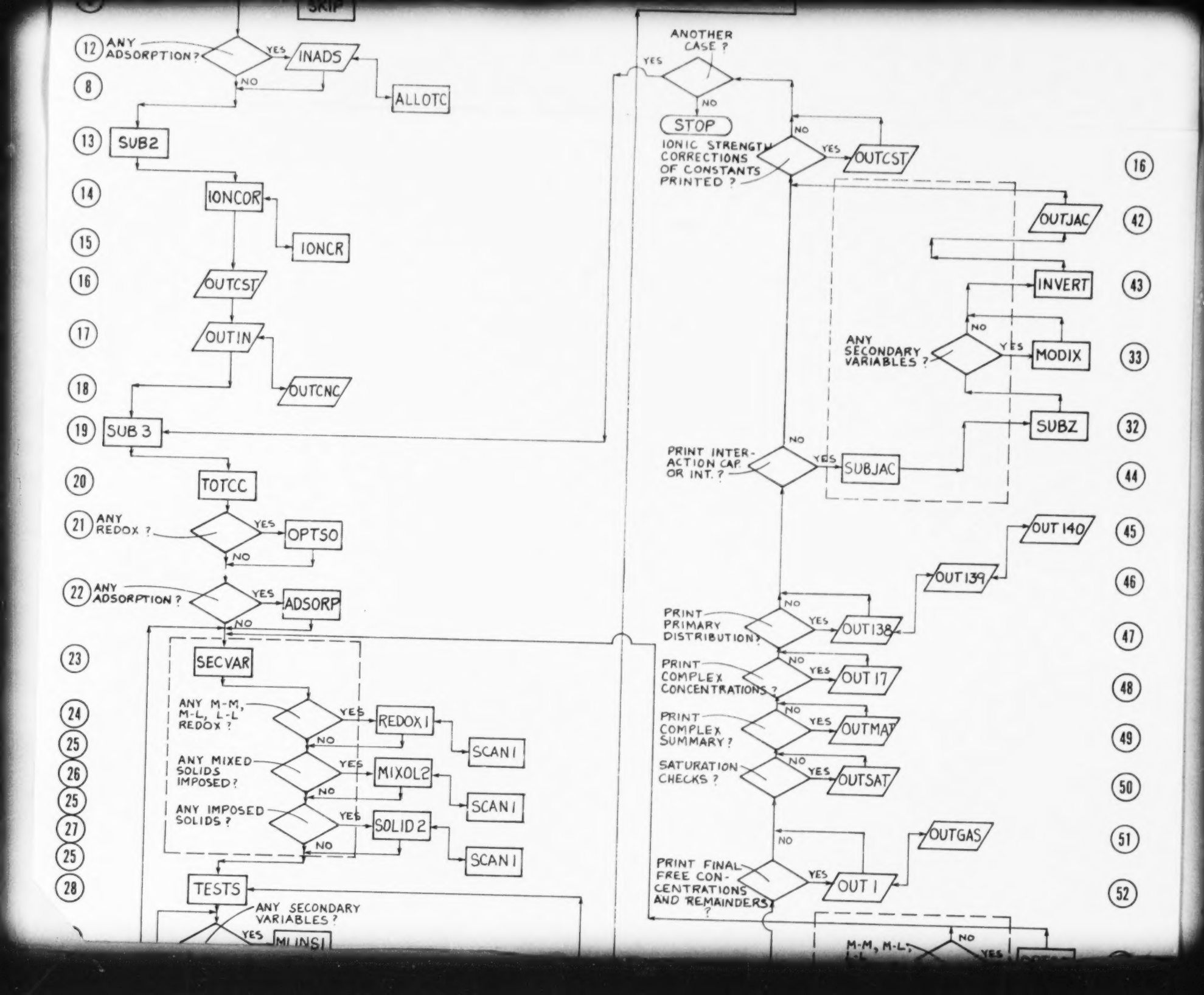

Reference Number
Guess free conc.
Case 1
Case 2
Case 3
Case 4
Case 5
Case 6
Case 7
Case 8
Case 9
Case 10
Metal Cards 3
mg/l input 3
--No. cards 3
equals num- 3
ber in col- 3
umns 2-3 on 3
header card 3
minus one. 3
Ligand Cards 4
mg/l input 4
--No. cards 4
equals num- 4
ber in col- 4
umns 5-6 on 4
header card 4
minus one. 4
OSU 2750

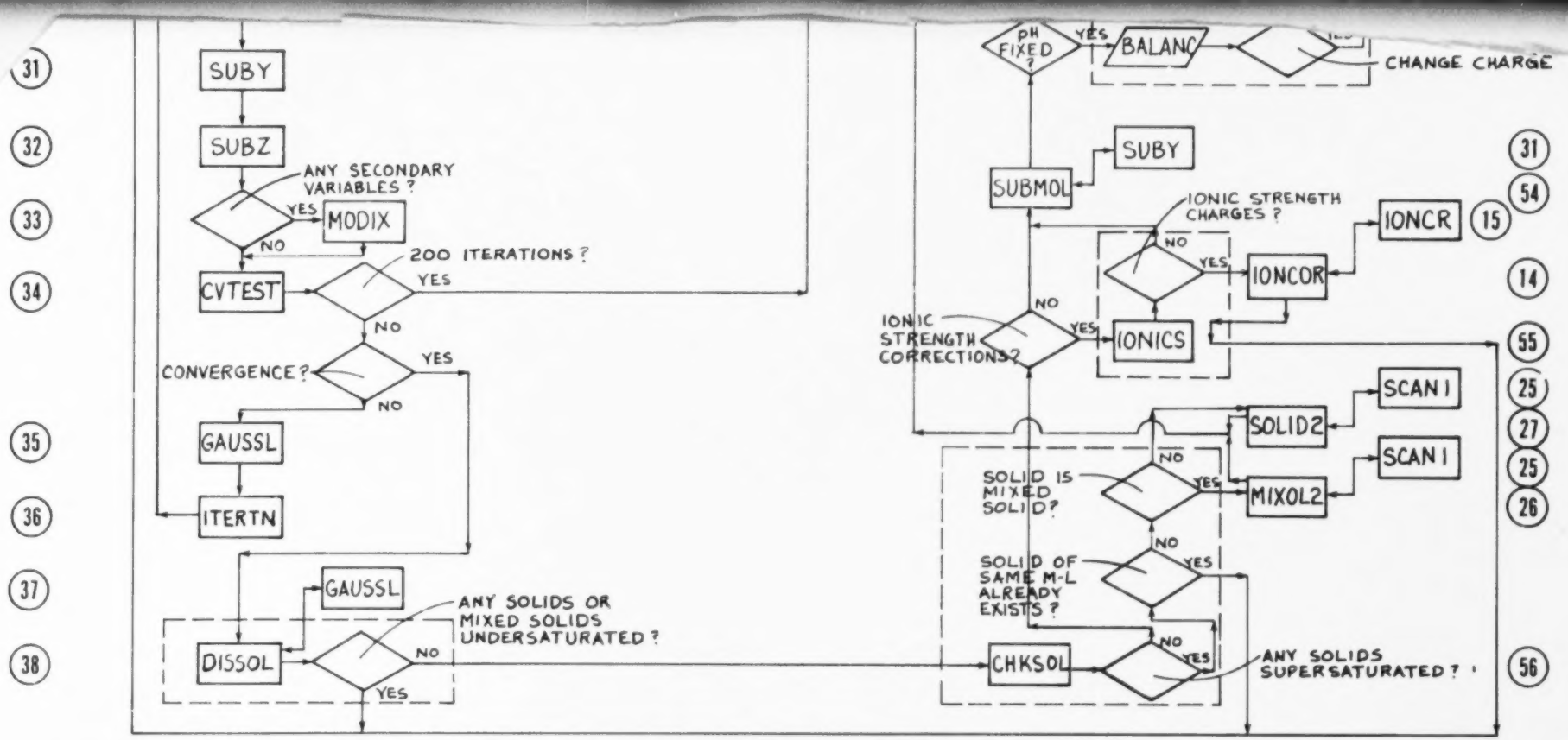

Reference Number
Guess free conc.
Case 1
Case 2
Case 3
Case 4
Case 5
Case 6
Case 7
Case 8
Case 9
Case 10
Ligand Cards 4
continued
mg/l input 4
4
4
4
4
4
4
4


Adsorbing surface cards --No. equals number in columns 17-18 on header cards 13
pH ZPC
log *K S a2
-log *K S a1
1 if *K S a1 given
Number of complexing metals
π
Metal adsorbtion cards --No. equals number in columns 24-25 of surface card 14
Reference number of metal
Number of complexes
100 X log K for 1st complex
Stoichiometry of metal in 1st complex
Stoichiometry of surface in 1st complex
Stoichiometry of H+ in 1st complex
100 X log K for 2nd complex
Stoichiometry of metal in 2nd complex
Stoichiometry of surface in 2nd complex
Stoichiometry of H+ in 2nd complex
100 X log K for 3rd complex
Stoichiometry of metal in 3rd complex
Stoichiometry of surface in 3rd complex
Stoichiometry of H+ in 3rd complex


pH_ZPC
log* K^S_a2
-log* K^S_a1
1 if *K^S_a1 given
Number of complexing metals
α
Adsorbing surface cards
Reference number of metal
Number of complexes
100 X log K for 1st complex
Stoichiometry of metal in 1st complex
Stoichiometry of surface in 1st complex
Stoichiometry of H+ in 1st complex
100 X log K for 2nd complex
Stoichiometry of metal in 2nd complex
Stoichiometry of surface in 2nd complex
Stoichiometry of H+ in 2nd complex
100 X log K for 3rd complex
Stoichiometry of metal in 3rd complex
Stoichiometry of surface in 3rd complex
Stoichiometry of H+ in 3rd complex
Metal adsorption cards
Ads. surf. cds.
Metal adsorption cards


1
XIGNAL
2
SUBI
3
INMAT
4
INCONC
5
ANY METALS OR LIGANDS ?
YES
DEFALT
NO
6
SKIP
7
ANY METAL LIGAND PAIR HAVE ALLOWED SOLID ?
YES
ALLOTS
NO
8
ANY METAL LIGAND PAIR HAVE A COMPLEX ?
YES
ALLOTC
NO
ANY REDOX COMPLEXES ?
9
INRED
ANY REDOX ?
YES
YES
NO
NO
8
ALLOTC
6
SKIP
ANY MIXED SOLIDS?
11
INMIX
YES
NO
6
SKIP
12
ANY ADSORPTION?
YES
INADS
NO
8
ALLOTC
13
SUB2
STOP
48
OUT17
NO
SATURATION CHECK ?
YES
OUTSAT
50
OUTCST
16
OUTGAS
51
OUT1
52
SUBY
31
SUBMOL
54
GAUSSL
37
DISSOL
38
ANOTHER CASE ?
YES
NO
STOP
NO
IONIC STRENGTH CORRECTIONS OF CONSTANTS PRINTED ?
YES
OUTCST
16


SKIP
12
ANY ADSORPTION?
YES
INADS
ALLOTC
NO
8
13
SUB2
14
IONCOR
IONCR
15
16
OUTCST
17
OUTIN
OUTCNC
18
19
SUB 3
20
TOTCC
21
ANY REDOX ?
YES
OPTSO
NO
22
ANY ADSORPTION ?
YES
ADSORP
NO
23
SECVAR
24
ANY M-M, M-L, L-L REDOX ?
YES
REDOX1
NO
SCAN1
25
26
ANY MIXED SOLIDS IMPOSED?
YES
MIXOL2
NO
SCAN1
25
27
ANY IMPOSED SOLIDS ?
YES
SOLID 2
NO
SCAN1
25
28
TESTS
ANY SECONDARY VARIABLES ?
YES
MLINS1
ANOTHER CASE ?
YES
NO
STOP
IONIC STRENGTH CORRECTIONS OF CONSTANTS PRINTED ?
NO
YES
OUTCST
16
OUTJAC
42
INVERT
43
ANY SECONDARY VARIABLES ?
NO
YES
MODIX
33
SUBZ
32
PRINT INTER-ACTION CAP. OR INT. ?
NO
YES
SUBJAC
44
OUT 140
45
OUT 139
46
PRINT PRIMARY DISTRIBUTION?
NO
YES
OUT138
47
PRINT COMPLEX CONCENTRATIONS ?
NO
YES
OUT 17
48
PRINT COMPLEX SUMMARY?
NO
YES
OUTMAT
49
SATURATION CHECKS ?
NO
YES
OUTSAT
50
NO
OUTGAS
51
PRINT FINAL FREE CON-CENTRATIONS AND REMAINDERS ?
YES
OUT 1
52
M-M, M-L,
NO
YES



K E Y

1. Called by MAIN to print information about program.
2. Initializes program variables according to instructions in the USGR Data Deck.
3. Reads through USGR Data Deck up to and including saturation card.
4. Reads metal and ligand concentrations and relates them to the data in the thermodynamic file.
5. Assigns default values if any case has a zero value.
6. Skips over records in thermodynamic deck.
7. Allots spaces for solids.
8. Allots spaces for complexes.
27. Defines secondary variable for imposed solid.
28. Computes TESTY, the vector of test values used in testing covergence.
29. Calculates concentration of each secondary variable.
30. Computes the concentration of each complex.
31. Computes error vector.
32. Computes matrix Z.
33. Modifies error vector and Z for the presence of secondary variables.
34. Tests error vector for convergence to zero.
35. Solves system of equations.

4. Reads metal and ligand concentrations and relates them to the data in the thermodynamic file.

5. Assigns default values if any case has a zero value.

6. Skips over records in thermodynamic deck.

7. Allots spaces for solids.

8. Allots spaces for complexes.

9. Correlates the redox reactions named by the USGR to detain thermodynamic file.

11. Correlates mixed solids named by user to data in the thermodynamic file.

12. Reads in adsorption cards.

13. Prints out conditions prior to case one, prints thermodynamic data, makes initial ionic strength corrections, summarizes User Data Deck.

14. Calculates constant part of Davies equation used to correct formation constants for ionic strength.

15. Makes ionic strength corrections.

16. Reports thermodynamic data for solids, complexes, redoxes and mixed solids.

17. Summarizes and prints the contents of the User Data Deck.

18. Summarizes concentrations of metals and ligands in the system.

19. Oversees completion of current case.

20. Updates total concentrations, pH and CO_2 status.

21. Adjusts formation constants for redox complexes and solids, adjusts TOTH for H^+ involved in REDOX.

22. Corrects, for changes in pH, apparent formation constants for complexes involving absorbing surfaces.

23. Assigns secondary variable for each redox, imposed mixed solid, or imposed solid.

24. Adds secondary variable for M-M, or L-L redox.

25. Searches secondary variable candidates and makes the variable with the lowest free concentration the new secondary variable.

26. Defines secondary variable for imposed mixed solid.

30. Computes the concentration of each complex.

31. Computes error vector.

32. Computes matrix Z.

33. Modifies error vector and Z for the presence of secondary variables.

34. Tests error vector for convergence to zero.

35. Solves system of equations.

36. Computes vector of corrected free concentrations.

37. Solves equations for solid concentrations.

38. Computes and stores concentrations of imposed solids, and mixed solids. Dissolves most undersaturated solids.

42. Prints interaction capacities or intensities.

43. Inverts the Z matrix.

44. Controls computation and printing of interaction capacities and intensities.

45. Prints primary distribution of species as a percentage.

46. Reports primary distribution of species as a percentage.

47. Calls OUT139 for appropriate data.

48. Prints concentration of each complex.

49. Prints complex summary.

50. Reports degree of saturation for each solid named on saturation card.

51. Computes and reports pO_2 and pN_2.

52. Reports pH, pE, TOTH, etc., plus all concentrations at end of case.

53. Computes charge on solution: varies no, one, or all ligand concentrations to obtain electroneutrality.

54. Computes final solid concentrations and the remainder vector.

55. Computes new ionic strength.

56. Precipitates most supersaturated solid or mixed solid. Adjusts coex matrix for new secondary variable.

...tection Agency
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use, $300

Fees Paid
Environmental
Protection
Agency
EPA-335

Special Fourth-Class Rate
Book

Please make all necessary changes on the above label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐, detach, or copy this cover, and return to the address in the upper left-hand corner.

EPA-600/3-80-049

B414
10